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MMS 86-0118

Humic Substances Isolated from Surface Sediments: Analytical Characteristics

MMS U.S. Department of the Interior
Minerals Management Service
Atlantic OCS Region

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Humic Substances Isolated from Surface Sediments: Analytical Characteristics

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U.S. Department of the Interior
Minerals Management Service
Atlantic OCS Region

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ABSTRACT

The elemental compositions of humic and fulvic acids isolated from Mid-Atlantic Continental Shelf and Slope surface sediments indicated relatively hydrogen-rich humic substances, as evidenced by the average atomic hydrogen-to-carbon ratios of 1.33 and 1.36, respectively. The average hydrogen-to-carbon ratio of the protokerogen was slightly lower at 1.05. Infrared spectra of the humic and fulvic acids and protokerogens showed absorption bands attributed to: 1) CH_2 and CH_3 aliphatic groups; 2) carbonyl groups of predominantly carboxylic acids; and 3) amide groups. The $\delta^{13}C$ isotopic ratios of the humic and fulvic acids range from -21.2 to -23.8 per mil with an average of -22.4 per mil. These values were 1.4 per mil lighter than the reported mean $\delta^{13}C$ ratio for marine plankton. Pyrolysis-gas chromatographic patterns of humic acids and protokerogens show longer carbon chain lengths which are indicative of gas-condensate-to-oil prone, hydrogen-rich organic components. The humic substances in this study are believed to be derived primarily from a marine organic source and may be precursors in the formation of Type II kerogens. Abundant foraminiferal tests observed in many of the sediment samples further support a marine planktonic environment. The $\delta^{13}C$ ratios of the protokerogens averaged -25.2 per mil and were isotopically lighter than the humic and fulvic acids. This difference may result (1) from an input of reworked organic matter, (2) from a preferential loss of ^{13}C-enriched functional groups through isotopic fractionation of the organic matter during formation of the protokerogens, or (3) through acid hydrolysis of the less resistant organic matter during isolation of the protokerogens. A succession of fulvic acid to humic acid to protokerogen is a possible evolutionary pathway for a portion of the protokerogens identified in this study.

INTRODUCTION

That portion of the soil organic matter which is insoluble in organic solvents and consists of amorphous, brown to black, hydrophilic, acidic organic components has been termed humic substances (Schnitzer and Khan, 1972). Humic substances are the major organic constituents of soils and sediments and may represent more than 90 percent of the total organic matter in young sediments (Tissot and Welte, 1978).

On the basis of their solubility in acid and base, soil humic substances are operationally divided into humic acid, fulvic acid, and humin. Humic acid is defined as the base-soluble portion that is precipitated by acidification of the alkaline solution, and fulvic acid is the base-soluble portion that remains in solution after acidification (Schnitzer and Khan, 1972, p. 3; and 1978). The operational definitions employed by soil scientists have been extended to the organic matter of sediments (Tissot and Welte, 1978, p. 81), and the terms fulvic acid and humic acid are also used in this context in this study. Humin, as defined by Schnitzer and Khan (1972, 1978), refers to that portion of the organic matter which is insoluble in both base and acid, whereas humin as defined by Tissot and Welte (1978) is that portion of the organic matter which remains after the alkaline extraction of the humic and fulvic acids. The term protokerogen used by Philp and Calvin (1976) and Stuermer and others (1978) is used in this study in preference to the term humin. Protokerogen is defined in this study as that portion of the organic matter which is insoluble through both the alkaline and acidic treatment of the sediment. This operational definition of protokerogen is analogous to the definition of kerogen as used by Hunt (1979, p. 550). Tissot and Welte (1978, p. 88) further suggest that a major portion of the organic matter in young sediments which is insoluble in alkaline aqueous solution may be hydrolyzed and extracted by the HF-HCl demineralization technique as used for the isolation of humin by Khan and Sowden (1971), Riffaldi and Schnitzer (1972) and Durand and Espitalie (1976). The presence of the hydrolyzable fraction is suggested to be the main difference between the insoluble organic matter in young sediments and kerogen (Tissot and Welte, 1978). The term hydrolyzable carbon as used in this study refers to that portion of the organic matter which is insoluble in alkaline solution but is hydrolyzed and extracted during HF-HCl digestion.

Mid-Atlantic Continental Shelf and Slope surface sediments were collected during a Bureau of Land Management (BLM) environmental baseline cruise in the winter of 1977 (Burreson, 1979). The sediments in this study were chosen to sample depositional environments of the Mid-Atlantic Shelf and Slope and include transects across the shelf and slope in water depths which range from 34 to 690 m (fig. 1, table 1). These sediments were previously Soxhlet extracted with toluene and methanol, and the results of the hydrocarbon analyses were reported by Miller and others (1979a).

The purpose of this study was (1) to isolate fulvic acid, humic acid, and protokerogen from Mid-Atlantic Continental Shelf and Slope surface sediments, (2) to characterize the humic substances by the determination of the elemental and stable carbon isotopic compositions and infrared spectra, (3) to differentiate sources of the major portion of the humic material, and (4) to examine the possible relationship between fulvic acid, humic acid, protokerogen, and the formation of kerogens.

Previous Work

Humic substances have been extensively studied, although much remains to be learned about their origin, synthesis, chemical structure and reactions, and their functions in terrestrial and aquatic environments (Schnitzer and Khan, 1978). The literature of humic substances in soils has been summarized by Kononova (1966) and Schnitzer and Khan (1972, 1978). Otsuki and Hanya (1967) examined the infrared spectra of humic acids isolated from lacustrine sediment, and Ishiwitari (1973) extended the study to include open marine sediments. Nissenbaum and Kaplan (1972) determined the elemental and stable carbon isotopic compositions and visible and electron spin resonance (ESR) spectra of humic acids extracted from soils and sediments of various terrestrial, lacustrine, and marine environments. Stuermer and others (1978) compared the elemental and stable carbon isotopic compositions and ESR spectra of humic acids and protokerogens isolated from different soils and sediments. In general, humic acids that are derived mainly from terrestrial plant organic matter are hydrogen-poor. These humic acids also have low atomic hydrogen-to-carbon ratios, a low intensity of CH groups in the 2920-2850 cm^{-1} wavelength region of the infrared spectrum, and an isotopically light ^{13}C composition similar to higher plants. On the other hand, humic acids derived from organic matter that lacked major terrestrial input are hydrogen-rich, show an increased intensity of CH absorption in the infrared spectrum, and are isotopically heavier (Nissenbaum and Kaplan, 1972; Huc and others, 1975; Stuermer and others, 1978). Nitrogen isotope ratios have also been shown by Stuermer and others (1978) to be useful indicators of the nitrogen nutrient source and may be used to differentiate humic substances derived from marine and terrestrial sources on the basis of differences in the ^{15}N composition of the nitrates used by marine algae and the atmospheric nitrogen used by terrestrial plants.

Carbon, nitrogen, and hydrogen atomic and stable isotopic ratios of humic and fulvic acids and protokerogens are presented in appendix 1. The reference and a brief description of the information from the literature are included in the appendix.

Bordovskiy (1965) and Nissenbaum and Kaplan (1972) observed that the atomic H/C ratios of humic substances derived largely from terrestrial organic matter were lower than the H/C ratios of humic materials derived from marine organic matter. Stuermer and others (1978) also suggested that the N/C ratios of humic substances from marine sources were generally higher than those from terrestrial sources. It is believed, however, that the atomic O/C ratios are not related to the organic source material but rather to a loss of oxygen during alteration and formation of the humic substances (Stuermer and others, 1978). The S/C ratios are believed to correlate to the redox conditions of the depositional environment rather than to the organic source material (Stuermer and others, 1978). From sulfur isotopic data, Nissenbaum and Kaplan (1972) concluded that, rather than being present in the original organic material, sulfur is incorporated into the sedimentary humic substances during diagenesis.

Differences were observed between the oxygen content of fulvic acid, humic acid, and protokerogen isolated from the same soil (Khan and Schnitzer, 1972; Riffaldi and Schnitzer, 1972). It is important to note, however, that there are apparently no data available on all three humic fractions isolated from the same sediment. Khan and Schnitzer (1972) and Riffaldi and Schnitzer (1972) suggested that fulvic and humic acids lose oxygen functional groups during diagenetic alteration. Debyser and others (1977b) further observed a decrease in the oxygen content of protokerogen with increasing depth.

The $\delta^{13}C$ isotopic ratios of humic substances may be used as an indicator of the source of the organic matter (Nissenbaum and Kaplan, 1972; Nissenbaum, 1974). The $\delta^{13}C$ ratios of estuarine sediments measured by Sackett and Thompson (1963) showed a gradation from -27 per mil for river sediments to -19 per mil for sediments from the open Gulf of Mexico. The authors concluded that the most probable explanation for this gradation was a decreasing influence of terrestrial organic carbon relative to marine organic carbon. Stuermer and others (1978) suggested that the use of the atomic H/C ratio in combination with the $\delta^{13}C$ isotopic ratio, might be more reliable than the use of either elemental ratios or isotopic evidence alone.

It has been suggested by Tissot and Welte (1978, p. 84) that increased polycondensation accompanied by elimination of hydrophilic functional groups leads to a decreased solubility of the organic material; the organic matter evolves from fulvic acid to the humic acid type and then to completely insoluble humin or protokerogen. The formation of humic substances is generally believed to result from the random condensation and polymerization of mixtures of biopolymers (such as peptides, carbohydrates, and lignin), the degradation products of the biopolymers, and other monomeric materials such as lipids (Schnitzer and Khan, 1972; Larter and Douglas, 1980). This generalized description of the formation of humic substances as proposed by Larter and Douglas (1980) carries two key words which relate to the complexity of the humic material, that is (1) random condensation and polymerization, and (2) mixtures of biopolymers, their degradation products, and other monomeric materials. Both terms imply the formation of complex and heterogeneous organic molecules, which suggests that no two humic substances will have identical structures. Wilson and Goh (1981) further believe that humic extracts vary considerably in chemical structure from sample to sample. The condensation and polymerization reactions may, however, result in humic substances with many structural similarities.

Schnitzer and Khan (1972) have summarized a great deal of the functional group and structural component data obtained from chemical degradation studies of humic substances. Recent nuclear magnetic resonance spectroscopic analyses have resulted in more direct evidence and confirmed many of the results discussed by Schnitzer and Khan (1972) (Grant, 1977; Wilson and others, 1978; Dereppe and others, 1980; Hatcher and others, 1980a, b, and c, and 1981; Wilson and Goh, 1981; Harvey and others, 1982). A highly branched and cross-linked network of aliphatic and alicyclic structures with varying degrees of aromatic components appears to form the basic, complex framework of humic substances (Grant, 1977; Hatcher and others, 1980a and b). Humic substances have oxygen-containing functional groups which include phenolic and alcoholic hydroxyls, carboxyls, carbonyls, and methoxyls, and nitrogen-containing amide linkages in their structures (Schnitzer and Khan, 1972). It has been observed that the major difference between humic substances isolated from soils and sediments with chiefly higher plant organic matter input is that the "terrestrial" humic substances have a greater aromatic content than humic substances derived from a primarily marine source (Dereppe and others, 1980; Larter and Douglas, 1980).

Felbeck (1971) and Schnitzer and Khan (1972) listed four possible processes for the mode of formation of humic substances: (1) plant alteration; (2) chemical polymerization; (3) cell autolysis; and (4) microbial synthesis. According to the plant alteration concept, fractions of plant material that are resistant to microbial attack are altered only slightly to form humic substances. This type of plant material would include lignified tissues, pollen, and spores. The chemical polymerization process suggests that plant materials are microbially degraded to small molecules which the microbes use as carbon and energy sources. The microbes synthesize and excrete products such as phenols and amino acids which undergo chemical oxidation and polymerization to form humic substances. Cell autolysis suggests that humic substances are formed from the autolysis products of plant and microbial cells after their death. The humic substances are formed by random condensation and free radical polymerization of cellular components such as sugars, lipids, and phenols. In the microbial synthesis mechanism, microbes use plant material as carbon and energy sources, synthesize humic-like substances intracellularly, and these high-molecular-weight substances are released after death of the microbes. The humic and fulvic acids are then formed by extracellular degradation of the high-molecular-weight compounds.

An additional concept, proposed by Maillard (1912) and discussed in detail by Manskaya and Drozdova (1968) and Hoering (1973) involves the formation of humic substances through melanoidin-type reaction pathways. This hypothesis incorporates aspects of the chemical polymerization and cell autolysis pathways as proposed by Felbeck (1971) and Schnitzer and Khan (1972). Larter and Douglas (1980) extended the melanoidin-type formation pathway to include lipid materials in the amino acid-sugar reaction mixture. Larter and Douglas (1980) reported that phytol may be incorporated into the structure and suggested that this reaction may be important to the fate of isoprenoid structures in the geosphere and may further relate to the presence of the isoprenoid structures in kerogen and petroleum.

Harvey and others (1982) have proposed a mechanism which involves oxidative cross-linking of polyunsaturated fatty acids to form marine fulvic and humic acids. This proposed pathway would apparently result in a structure which is consistent with the nuclear magnetic resonance (NMR) data for a highly branched and cross-linked framework of aliphatic and alicyclic structures and is also consistent with many of the observed physical and chemical properties of humic substances.

In this study, elemental, carbon isotopic, infrared spectroscopic and pyrolysis-gas chromatographic analyses were carried out on bulk humic substances and, as such, are believed to provide basic framework information on the major organic sources of the humic materials. The humic substances in these Holocene sediments are believed to be formed from organic matter derived from various sources which include marine plankton and bacteria, terrestrial plants and microorganisms associated with the plant detritus, as well as reworked sedimentary carbon. These analyses which are performed on bulk humic substances are considered as a qualitative measure of the dominant organic input. Visual microscopic analyses of the protokerogens are included to further characterize the types of organic matter present.

Methods

The sediments were initially treated with 0.2 N HCl to remove carbonates and were dried under a stream of nitrogen. The fulvic and humic acids were extracted from the sediment with 0.5 N NaOH after the method of Schnitzer and Khan (1972). The sediment was placed in glass jars with a solution-to-sediment ratio of 10 ml of 0.5 N NaOH to 1 g sediment. Each jar was flushed with nitrogen, sealed with a lid, and then was decanted and centrifuged. Extraction of the sediment was repeated until no further fulvic or humic acids were extracted, as evidenced by a lack of yellow to brown color in the solution.

The extraction solutions which contained the fulvic and humic acids were combined, reduced in volume on a vacuum roto-evaporator, and passed through a chromatographic column of Dowex[1] 50 (H^+ form) exchange resin to remove cations. Humic acids precipitated under the acidic conditions of the column and were eluted with Nh_4OH. The extraction solution was adjusted to pH 2 by the addition of 2 N HCl after the cation exchange treatment and the precipitated humic acids were separated from the soluble fulvic acids by centrifugation. The humic acids were purified by dissolution in 0.5 N NaOH, followed by centrifugation to remove inorganic material which may have initially co-precipitated with the humic acids. The basic solution was again acidified and the precipitated humic acids were rinsed with distilled water to remove soluble salts and were freeze-dried. The ash content of the humic acids was less than 10 percent after this treatment. Soluble fulvic acids were reduced in volume, passed through a cation exchange column to reduce the salt content, and freeze-dried. The ash content of the fulvic acids ranged from about 40 to 80 percent at this point. The fulvic acids were redissolved in a minimum volume of 0.5 N NaOH and the pH adjusted to 7 by addition of 2 N HCl. A white or very light yellow precipitate formed in the neutral fulvic acid solutions and was analyzed by infrared spectroscopy and X-ray diffraction. The infrared spectra of the precipitate isolated from station G-5 fulvic acid was nearly identical with the spectra of silica gel. In addition, the X-ray diffraction pattern of the precipitate showed basal spacings at 2.50 and 2.96 A, and, although the pattern does not correspond precisely with sodium silicate, the material was believed to be an amorphous silicate (M.J. Pavich, oral commun., 1980). The solutions were centrifuged and the supernatant was placed in dialysis tubing and dialyzed against running distilled water for 36 to 48 hrs. A loss of low molecular weight fulvic acids may have occurred during this step. The fulvic acid solutions were passed through four to six successive chromatographic columns of ion exchange resin (modified from Holtzclaw and others, 1976). This additional treatment reduced the ash content to less than 10 percent in most of the fulvic acids.

Extraction of humic and fulvic acids from the sediment was also attempted by means of a combination of 0.1 N NaOH and 0.1 M $Na_4P_2O_7$, as described by Kononova and Bel'chikova (1961) and Schnitzer and Khan (1972). This method was reported to result in a yield of humic substances comparable to that of basic extraction and also to eliminate interference from carbonate in the sediment without prior HCl treatment (Kononova and Bel'chikova, 1961). The fulvic and humic acids extracted by the basic pyrophosphate technique were from station J-2 sediment and are designated J-2 #1. Although the elemental compositions and infrared spectra of the fulvic and humic acids extracted by both methods were similar, total recovery of the humic substances was much lower with the basic pyrophosphate method than with NaOH extraction. Schnitzer and Khan (1978) indicated that pyrophosphate was difficult to remove during purification of humic substances, and a large portion of the fulvic and humic acids extracted by the method in this study were lost as a result of attempts to remove the pyrophosphate during isolation and purification of the humic fractions.

The insoluble protokerogen which remained after NaOH extraction was isolated by dissolution of most of the inorganic material following the method described by Durand and Espitalie (1976) and Huc and Durand (1977). This method involved treatment of the residual sediment with 4 N HCl followed by repeated treatment with a mixture of 4 N HCl and 48 percent HF with an increasing strength of HF from 2/3 HCl-1/3 HF to 1/3 HCl-2/3 HF at 70° C. After dissolution and removal of the clays and silicates, the protokerogen was repeatedly rinsed using distilled water until the pH was 7, and then dried. At this point, the ash content of the protokerogen was still high in all of the samples and ranged from 51 to 64 percent.

Slightly soluble fluorides of Ca, Mg, and Fe as well as complex fluorides which contain more than one cation may form as a result of the HF-HCl digestion of the sediment during isolation of the insoluble protokerogen or kerogen fractions (Forsman and Hunt, 1958; Long and others, 1968). The x-ray diffraction pattern of the protokerogen isolated from station C-4 sediment showed basal spacings which included 1.77, 1.93, 2.89, 3.03, 3.09, and 5.75 A and which are believed to be consistent with the presence of a mixture of complex fluorides. Forsman and Hunt (1958) and Long and others (1968) suggested that fluorides may be removed by dissolution in saturated carbonate solutions, and Forsman and Hunt (1958) further pointed out that the use of $(NH_4)_2CO_3$ rather than Na_2CO_3 or K_2CO_3 would prevent the possibility of the additional formation of slightly soluble Na or K fluosilicates.

The protokerogen was thoroughly mixed with saturated $(NH_4)_2CO_3$ solution as modified from the methods of Forsman and Hunt (1958), Long and others (1968), and Saxby (1970). The solution was allowed to stand at room temperature for 24 h, centrifuged, and the supernatant was removed and discarded. The residue was again treated with saturated $(NH_4)_2CO_3$ solution at a temperature of 40-50° C for 1 h, the solution centrifuged and the supernatant decanted. The $(NH_4)_2CO_3$ procedure was repeated and the residue rinsed with hot distilled water (40-50° C) followed by treatment with 2 N HCl at a temperature of 40-50° C for 1 h. The residue was repeatedly rinsed with hot distilled water until the pH of the solution was 7. The protokerogen was dried for determination of the ash content and elemental and infrared spectroscopic analysis.

The moisture content of the fulvic acids, humic acids, and protokerogens was determined after drying an aliquot of the sample at 105° C for 16 h. Percent ash determinations were made after combustion of weighed aliquots of the humic substances at 950° C for 4 h.

Infrared spectroscopic analysis was performed using a Perkin-Elmer model 621 IR spectrograph and KBr discs. Known concentrations of the humic substance, approximately 0.8 mg of the fulvic and humic acids and 0.6 mg of the protokerogen, were added to 300 mg KBr, ground and mixed with a micro ball mill for 1 min, dried at 105° C for 15 min after grinding, and pressed into discs under vacuum at 15,000 lbf/in 2 for 10 min. The KBr discs were stored in a desiccator to insure a moisture-free environment. The discs were placed in mantles heated to 105° C to further minimize moisture interference during spectroscopic analysis and run against blank KBr discs treated in identical fashion. The instrumental conditions for analysis were as follows: a scan time of 13 min, attenuator speed of 1300, gain 4.9, and the slit program set at 1000. The balance of the instrument was checked frequently, and a polystyrene film was analyzed daily to check the accuracy of the recorded wavelengths. Slit width and grating changes were performed automatically as determined by the slit program.

Samples for total organic carbon determination were prepared for analysis as described by Miller and others (1979b). Total organic carbon percentages were determined by combustion of a weighed aliquot using a Perkin-Elmer model 240 Carbon Hydrogen Nitrogen Analyzer. Acetanilide was used to determine the K values (sensitivity in μV/μg) for carbon. Two sediment samples, which had been analyzed previously for total organic carbon content, were reanalyzed and the results are reported in table 2. The agreement between the two analyses showed a precision of 94 percent or greater.

Analysis of the carbon, hydrogen, and nitrogen elemental composition of the humic substances was also performed on the Perkin-Elmer CHN Analyzer. Sulfur contents were determined on a LECO SC-132 Sulfur Determinator. An aliquot of the humic substance was weighed, dried at 105° C, then reweighed to determine the moisture-free weight. The aliquot was held in the oven at

105° C until elemental analysis to minimize water interference with the hydrogen and oxygen determinations. Analyses were performed on duplicate aliquots. The data presented in tables 4, 5, and 6 have been corrected for the percent ash. The oxygen content was determined by summing the carbon, hydrogen, nitrogen, and sulfur percentages and subtracting this sum from 100 percent. Several other elements, which include Cl, Br, I, F, and P, are known to be present in humic substances but were not measured and would be included in the oxygen values.

Visual microscopic examination of the protokerogens showed the presence of round masses which consisted of particles with metallic luster and golden yellow color. In several cases a cubic form could be seen in larger particles and the masses were believed to be pyrite framboids (E. Robbins, oral communication, 1981).

Pyrite may be removed from protokerogens by several techniques which include oxidation with HNO_3 or reduction with $LiAlH_4$, $NaBH_4$, or Zn-HCl (Saxby, 1970). Saxby (1970) suggested that these treatments will alter the organic matter through oxidation or reduction. It was therefore preferable to correct for the effect of pyrite by determination of Fe and S, calculating the organic sulfur by the difference between total S and pyritic S after the method of Smith (1961) and Durand and Espitalie (1976). The assumption was made by this method that iron was present in the protokerogens entirely as FeS_2 and that the organic matter was composed of C,H,N,O, and S. Few minerals are resistant to the HF-HCl treatments used to isolate the protokerogen. Iron in the form of iron carbonates or present in silicate minerals would have been solubilized and removed during the acid treatment, although iron oxides may still be present. The assumption may also be supported by the possible presence of pyrite framboids in the protokerogens.

An aliquot of each protokerogen was treated with concentrated HNO_3 to oxidize iron sulfides and dissolve the iron (method after P. Aruscavage, oral communinication, 1981). The HNO_3 was evaporated on a steam bath and the sample transferred to a volumetric flask in 10 percent HCl. An iron standard was prepared using iron dust (99.9 percent pure), and dilutions were made with iron concentrations of 0.5 to 10.0 ppm. The standards and samples were analyzed at a wavelength of 248.3 nm on a Perkin Elmer Model 5000 Atomic Absorption Spectrophotometer equipped with a hollow cathode lamp light source, and an air-acetylene flame. A standard iron calibration curve was prepared by means of the absorbances of the standard iron dilutions. The iron concentrations of the protokerogens were determined using the sample absorbance readings compared to the standard calibration curve. The accuracy of the standard dilutions was checked by comparison with iron standards prepared by P. Aruscavage and the values agreed within 1.5 percent.

After the iron content of the protokerogens was measured, the organic sulfur was determined by the difference of total sulfur and iron sulfide sulfur, and the elemental composition corrected for the loss in weight caused by oxidation of the iron sulfide to iron oxide during elemental analysis (Smith, 1961; Durand and Espitalie, 1976). The copper content of protokerogens from stations C-4 and G-3 was also measured to correct for sulfur possibly present as chalcopyrite. The copper concentrations, however, were less than 2.5 percent of the iron concentrations and copper was not determined in the other protokerogens. It is possible that a portion of the iron sulfide may be present as chalcopyrite or marcasite, although the presence of framboids and the low copper content of the protokerogens suggests that pyrite may be the predominant form.

Acetanilide was used in the CHN analyses of the humic substances to determine the K values for carbon, hydrogen, and nitrogen. Benzoic acid and cyclohexanone-2,4-dinitro-phenylhydrazone were analyzed as unknowns. The oxygen content was determined by difference and the results of the carbon, hydrogen, nitrogen, and oxygen analyses were in excellent agreement with the known compositions (table 2). Blanks consisted of analysis of a ladle and platinum boat with no sample and were measured before and after each standard and sample analysis to insure quality control of the blank values.

A series of seven standard coals and cokes, which ranged in sulfur content from 0.42 to 3.63 percent, were analyzed on the LECO Sulfur Determinator to establish a calibration curve for the determination of the percent sulfur of the humic substances. A coefficient of linear correlation of 0.99 was determined for the regression analysis.

The humic substances isolated from the sediment from four stations, A-2, D-4, J-2, and K-5, were chosen for $\delta^{13}C$ isotopic analysis. These sediments were selected to represent the geographical and geological distribution of the stations and the range of lithologies and total organic carbon content of the sediments in this study. The samples were combusted at 900° C in a vacuum line similar to that of Craig (1953), and the CO_2 was purified before isotopic analysis as described by Degens (1969). The $^{13}C/^{12}C$ ratio of the CO_2 was measured with an isotope-ratio mass spectrometer, provided by T.B. Coplen, U.S. Geological Survey, Reston, Virginia. The ratios are expressed in parts per thousand (per mil) and reported in standard δ-notation of Craig (1953) referenced to the Peedee Belemite (PDB) standard by the following relationship:

$$\delta^{13}C = \frac{^{13}C/^{12}C \text{ sample}}{^{13}C/^{12}C \text{ standard}} - 1 \times 1000$$

Toluene-methanol extracted sediment samples and humic substances isolated from the sediment from four stations (G-5, G-6, J-2 and K-4) were chosen for

Table 2 - Accuracy of total organic carbon and carbon, hydrogen, and nitrogen elemental determinations

	Sample		Measured	Actual	Accuracy
			Percent		
Total Organic Carbon Determination:					
	Barnegat Bay #1 -	C	0.17	0.18*	94.4
	Tenneco 642-2 - (1910-2090 ft.)	C	0.45	0.46*	97.8
Carbon, Hydrogen, Nitrogen Elemental Analyses:					
	Benzoic Acid -	C	68.87	68.85	99.97
		H	4.97	4.95	99.60
		O	26.16**	26.20	99.80
	Cyclohexanone-2, 4-dinitro-phenyl-hydrazone -	C	51.79	51.79	100.00
		H	5.18	5.07	97.88
		N	19.74	20.14	98.01
		O	23.29**	23.00	98.75

*Data previously determined by H. E. Lerch, U.S. Geological Survey.

**By difference.

pyrolysis-gas chromatographic analysis by Geochem Research, Inc., under contract #14-12-0001-30106. The thermal breakdown products were evolved by heating of the sample material to a maximum temperature of 600° C. Gas chromatographic analysis of the thermal pyrolysate was performed on a 30 m fused silica glass capillary column coated with DB-5 liquid substrate. The gas chromatographic column was held at 50° C for four (4) min. then temperature-programmed at a rate of 16° C/min. to a final temperature of 300° C.

DEPOSITIONAL ENVIRONMENTS AND STATION LOCATIONS

The modern Middle Atlantic Outer Continental Shelf is a tectonically stable platform which is underlain by an elongate structural basin, the Baltimore Canyon Trough. The trough trends northeast and extends from the Long Island Platform southwestward to Chesapeake Bay (Knebel, 1979). The Baltimore Canyon Trough has been studied in conjunction with oil and gas exploration efforts (Scholle, 1977, 1980) and the stratigraphy of the trough has recently been summarized by Schlee (1981). No physiographic expression of the basin is apparent on the smooth, wide, gently-dipping plain that forms the continental shelf (Knebel, 1979).

The depositional environments may be characterized as a predominantly oxygenated marine environment with a relatively low rate of deposition. The water column which overlies the shelf becomes weakly stratified thermally during the summer, and the oxygen content, which is saturated or super-saturated in the near-surface water, may be reduced at depth, especially in the sewage dump site of the New York Bight area (Segar and Berberian, 1976). The dominant source of sediment for the shelf is believed to be Pleistocene deposits underlying the surficial sediments (Swift, 1969). The rivers adjacent to the Baltimore Canyon Trough area drain a glacial terrain and transport very little sediment onto the shelf (Reineck and Singh, 1980, p. 375). Further-more, estuarine systems are believed to trap much of the sediment carried by the rivers, although sediment may be periodically swept onto the shelf by storm-related processes (Reineck and Singh, 1980, p. 376). Rapid transgressions and regressions of the sea during glacial episodes have resulted mainly in relict sediments on the shelf, which denote that the sediments may have been deposited under conditions different from the present environments (Reineck and Singh, 1980, p. 374). It is believed that these relict sediments in the Baltimore Canyon Trough area are being reworked under present conditions by processes which include waves, tidal currents, benthic organisms, wind-driven currents, internal waves, and canyon-related currents (Knebel and Folger, 1976).

The morphology of the shelf in the Baltimore Canyon Trough region has been reviewed by Swift and others (1976). The bottom is typically covered by paired linear ridges and depressions, or swales, that are 2 to 6 km wide and 12 to 54 km long with a relief of 2 to 6 m (Knebel and Folger, 1976). Surficial sediments in the Baltimore Canyon Trough area have been shown to be primarily medium-grained sands, although patches of fine-grained sand extend across the shelf off both northern and southern New Jersey and along the shelf break (Knebel and Spiker, 1977; Knebel, 1979).

Stations for the BLM's Middle Atlantic environmental benchmark studies were chosen as representative of bathymetric zones and reflective of high interest in oil and gas exploration (Burreson, 1979). The sediments for this present study were selected from the sampling areas and transects of the BLM study (fig. 1, table 1).

Area A of the BLM study covered a relatively gently sloping portion of the outer shelf and shelf break south of Hudson Canyon (Burreson, 1979). Four stations, B-1, C-4, D-4, and E-2 in this study represented the ridge,

Table 1 - Location of sampling stations and description of surface sediment collected from Mid-Atlantic study sites.

Sample	Station	Location	Water Depth (m)	Description of Sediment
A	A-2	39°22.2' N 72°31.0' W	127	Silty, medium-fine quartz sand, about 25 percent silt and clay, shell fragments noted, abundant foraminiferal tests with occasional siliceous radiolaria, trace micas.
B	B-1	39°19.3' N 73°10.1' W	63	medium quartz sand, few small shell fragments and forams, trace feldspars.
C	C-4	39°15.2' N 74°08.0' W	34	medium-fine quartz sand, few small shell fragments and forams, trace micas, coal.
D	D-4	39°02.9' N 73°47.2' W	49	fine quartz sand, about 5 percent silt and clay, occasional forams, trace micas, feldspars, coal.
E	E-2	38°44.2' N 73°25.5' W	73	medium-fine quartz sand, with large shell fragments and occasional forams noted, less than 5 percent silt and clay.
F	F-2	38°44.2' N 73°09.1' W	110	fine quartz sand, abundant forams and few radiolarians.
G	G-3	39°43.7' N 72°54.7' W	73	mixed quartz sand with numerous coarse, rounded quartz grains, about 5-10 percent silt and clay, abundant shell fragments, few forams.
H	G-5	39°48.9' N 72°12.3' W	90	medium-fine quartz sand, about 10 percent silt and clay, numerous shell fragments, occasional forams and radiolarians.
I	G-6	39°40.6' N 72°00.8' W	167	fine quartz sand, very abundant forams and a few radiolarians.
J	J-2	38°45.6' N 72°59.0' W	690	clayey silt, 95 percent silt and clay, 5 percent quartz sand, abundant forams and occasional radiolarians, trace shell fragments and micas.
K	K-4	38°04.5' N 74°01.7' W	105	fine quartz sand, about 5 percent silt and clay, very abundant shell fragments and forams, trace micas, radiolaria.
L	K-5	38°01.6' N 73°53.8' W	151	fine quartz sand, about 10 percent silt and clay, very abundant forams and occasional radiolarians, few shell fragments.
M	K-6	38°00.8' N 73°51.8' W	350	very fine quartz sand, about 20 percent silt and clay, very abundant forams and few radiolarians, trace micas.

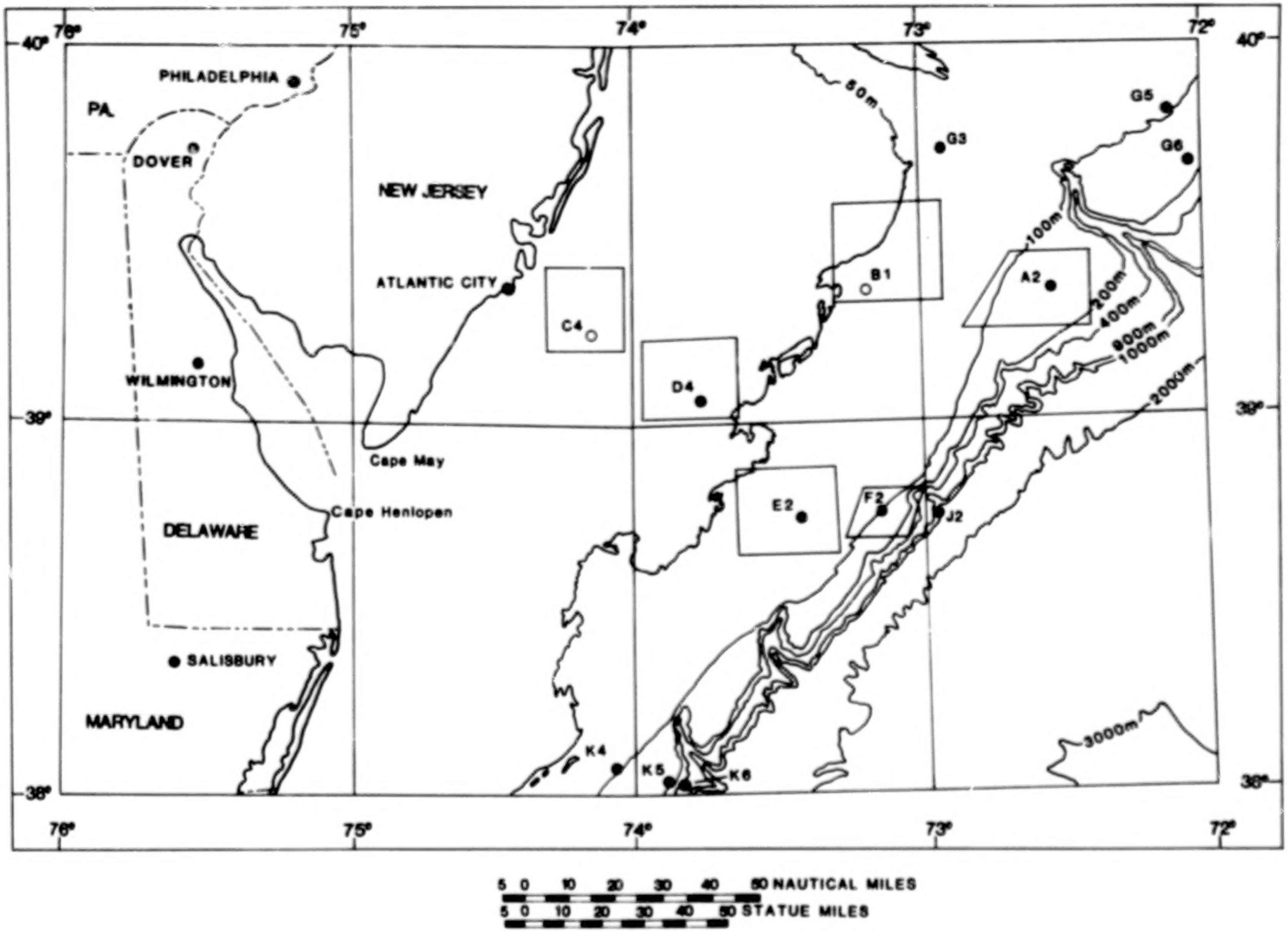

Figure 1.--Station locations of Mid-Atlantic Shelf and Slope surface sediments.

flank, and swale topography of the shelf. Area B included ridges and swales in 56 to 74 m of water (Burreson, 1979). Station B-1 was a flat area in the ridge and swale topography. Well-developed ridge and swale topography was sampled in the inner shelf area C in water depth of 15 to 35 m and in the central shelf area D in the 30 to 50 m depth range (Burreson, 1979). Stations C-4 and D-4 represented swales in these areas. Area E covered outer shelf ridge and swale topography (55 to 90 m water depth) north of the head of Wilmington Canyon (Burreson, 1979). Area F was an outer shelf-break sampling area which showed a much steeper depth gradient and sediments which contained less silt and clay than area A.

Transect G, stations G-3, G-5, and G-6, extended from the axis of the Hudson Shelf Valley, across the valley to the shelf break north of Hudson Canyon. Transect K, stations K-4, K-5, and K-6, extended across the shelf to the upper slope south of Baltimore Canyon. The shelf stations were located on flat or flank bottoms, and topographic highs and lows were avoided in order to minimize the effect of topography on apparent cross-shelf patterns (Burreson, 1979). Station J-2 was located on the slope west of area F.

RESULTS AND DISCUSSION

Total Organic Carbon

The distribution of carbon in the humic fractions relative to the total organic carbon content of the sediment is presented in table 3. Total organic carbon (TOC) values were determined on sediment which had previously been extracted with solvents and do not include the organic solvent soluble portion of the organic carbon. The TOC content was below 0.40 percent for each of the sediment samples with the exception of a value of 1.83 percent C determined for the sediment from station J-2. Burreson (1979) suggested that the organic carbon content is closely related to the distribution of silt and clay in

Table 3 - Fulvic acid, humic acid, protokerogen and hydrolyzable carbon expressed as percentages of the total organic carbon

		Total Organic Carbon	Fulvic Acid	Humic Acid	Humin	Hydrolyzable* Carbon
Sample	Station	(Percent)				
A	A-2	0.38	2.89	5.07	33.45	58.59
B	B-1	0.07	4.34	3.77	19.81	72.08
C	C-4	0.09	7.05	5.40	51.52	36.03
D	D-4	0.09	6.51	4.82	41.91	46.76
E	E-2	0.12	10.20	5.21	59.14	25.45
F	F-2	0.15	0.27	4.91	31.93	62.89
G	G-3	0.20	5.31	3.37	79.37	11.95
H	G-5	0.29	9.03	10.62	37.43	42.92
I	G-6	0.22	7.23	26.75	44.78	21.24
J	J-2	1.83	3.62	13.14	35.04	48.20
K	K-4	0.19	14.78	19.05	29.94	36.23
L	K-5	0.27	3.76	11.42	25.08	59.74
M	K-6	0.18	9.12	18.79	70.92	1.17

*By difference.

the Mid-Atlantic sediments. The results reported here suggest that, in addition to grain size, the TOC may also be related to the abundance of foraminiferal tests (tables 1,3).

The shelf sediments showed a generally low organic richness with an average TOC value of 0.17 percent. It is suggested that the organic matter in the Mid-Atlantic is repeatedly subjected to chemical oxidation and biological degradation which results in the low organic carbon values. This interpretation is based on the low rate of sediment deposition on the shelf, an oxygenated water column, and evidence for resuspension and reworking of the sediments in the Baltimore Canyon Trough area as noted by Reineck and Singh (1980). The TOC content of the Mid-Atlantic Slope sediment from station J-2 was considerably higher, 1.83 percent, than the Shelf sediments, which may reflect a greater rate of preservation of the organic matter possibly due to a lower oxygen content in the water column and greater rate of sediment deposition.

Elemental Analyses

The results of the elemental analysis of the fulvic acids isolated from the sediments are given in table 2 on a dry, ash-free basis. The carbon content of the fulvic acids ranged from 34.2 to 44.0 percent, and the hydrogen, nitrogen, and oxygen by difference ranged from 3.5 to 5.6 percent, 2.4 to 7.7 percent, and 46.2 to 58.8 percent, respectively. Sulfur was not determined due to analytical difficulties. A loss of low molecular weight fulvic acids may also have occurred during dialysis and represents a limitation to the interpretation. The atomic H/C ratios of the fulvic acids in this study varied from 1.11 to 1.60, the O/C ratios ranged from 0.82 to 1.29, and the range of the N/C ratios was 0.052 to 0.195 (table 4). When the atomic ratios are plotted in van Krevelen type diagrams and compared with the literature data, the fulvic acids generally showed H/C, O/C, and N/C ratios similar to sediments from

Table 4 - Elemental composition and atomic ratios of fulvic acids isolated from Mid-Atlantic surface sediments by extraction with 0.5 N NaOH

Sample	Station	Ash Percent	Elemental Composition, In Percent (Ash-free Basis)				Atomic Ratios		
			%C	%H	%N	%O*	H/C	O/C	N/C
A	A-2	6.6	38.73	4.25	2.36	54.66	1.31	1.06	0.052
B	B-1	4.7	41.41	5.57	5.95	47.07	1.60	0.85	0.123
C	C-4	2.4	39.93	5.23	3.74	51.10	1.56	0.96	0.080
D	D-4	4.6	40.32	4.95	5.40	49.33	1.46	0.92	0.115
E	E-2	13.8**	34.23	3.53	3.46	58.78	1.23	1.29	0.087
F	F-2	2.7	40.90	5.28	4.70	49.12	1.54	0.90	0.099
G	G-3	19.0**	40.50	4.14	9.21	46.15	1.22	0.86	0.195
H	G-5	5.0	44.00	4.11	3.60	48.29	1.11	0.82	0.070
I	G-6	9.2	41.21	4.40	5.19	49.20	1.27	0.90	0.108
J	J-2	5.5	35.28	4.30	3.56	56.86	1.45	1.21	0.087
	J-2 #1***	5.8	43.15	4.57	2.94	49.34	1.26	0.86	0.058
K	K-4	4.6	36.80	4.51	5.17	53.52	1.46	1.09	0.121
L	K-5	18.5[2]	38.76	3.96	5.59	51.69	1.22	1.00	0.124
M	K-6	14.8[2]	39.18	4.58	7.68	48.56	1.39	0.93	0.168

*By difference.

**Insufficient sample remained for further reduction of ash content.

***Method of extraction was by a combination of $NaOH-Na_4P_2O_7$.

Lakes Ontario and Erie (samples 99, 101, 103) the Cariaco trench (sample 9) and the Emerald Basin (sample 6) as well as soils (samples 85, 119, 123, 140, 179, 281) from various locations (figs. 2-4, appendix 1).

The presence of silica as a component of the inorganic content of the fulvic acids may be a result of the alkaline dissolution and leaching of silica from siliceous planktonic tests, from silicate minerals such as feldspars or micas or, least likely, from the glass containers used for the extraction. Griffith and Schnitzer (1975) isolated fulvic acids from volcanic soils which developed from andesite composed chiefly of Na-rich plagioclase feldspars. These authors were able to reduce the ash content of the fulvic acids to only 9 to 13 percent, due to silica associated with the fulvic acids. Nissenbaum and Swaine (1976) further suggested that the association of silica with humic substances may occur naturally. It was also shown by Schnitzer (1969) that fulvic acids form associations with metals, and the ash content of the fulvic acids in this study may be in part a result of this type of association.

The inorganic material present in the fulvic acid fraction may affect elemental analyses (Malcolm, 1976). Schnitzer and Kodama (1972) observed that fulvic acid was so tightly held by a Cu^{2+}-silicate clay that greater than three-fourths of the total fulvic acid resisted decomposition, even when heated to 1000° C. This mechanism would result in elemental analysis in which only a portion of the fulvic acid had been combusted. Combustion of the fulvic acids during elemental analysis may also release water bound to the amorphous silica and may result in positive errors in the determination of the oxygen and hydrogen contents (Malcolm, 1976). Both mechanisms may give a lower observed carbon content and higher oxygen content of the fulvic acids than actually present and may also have resulted in the relatively low hydrogen contents (3.5 - 5.6 percent) noted in these fulvic acids.

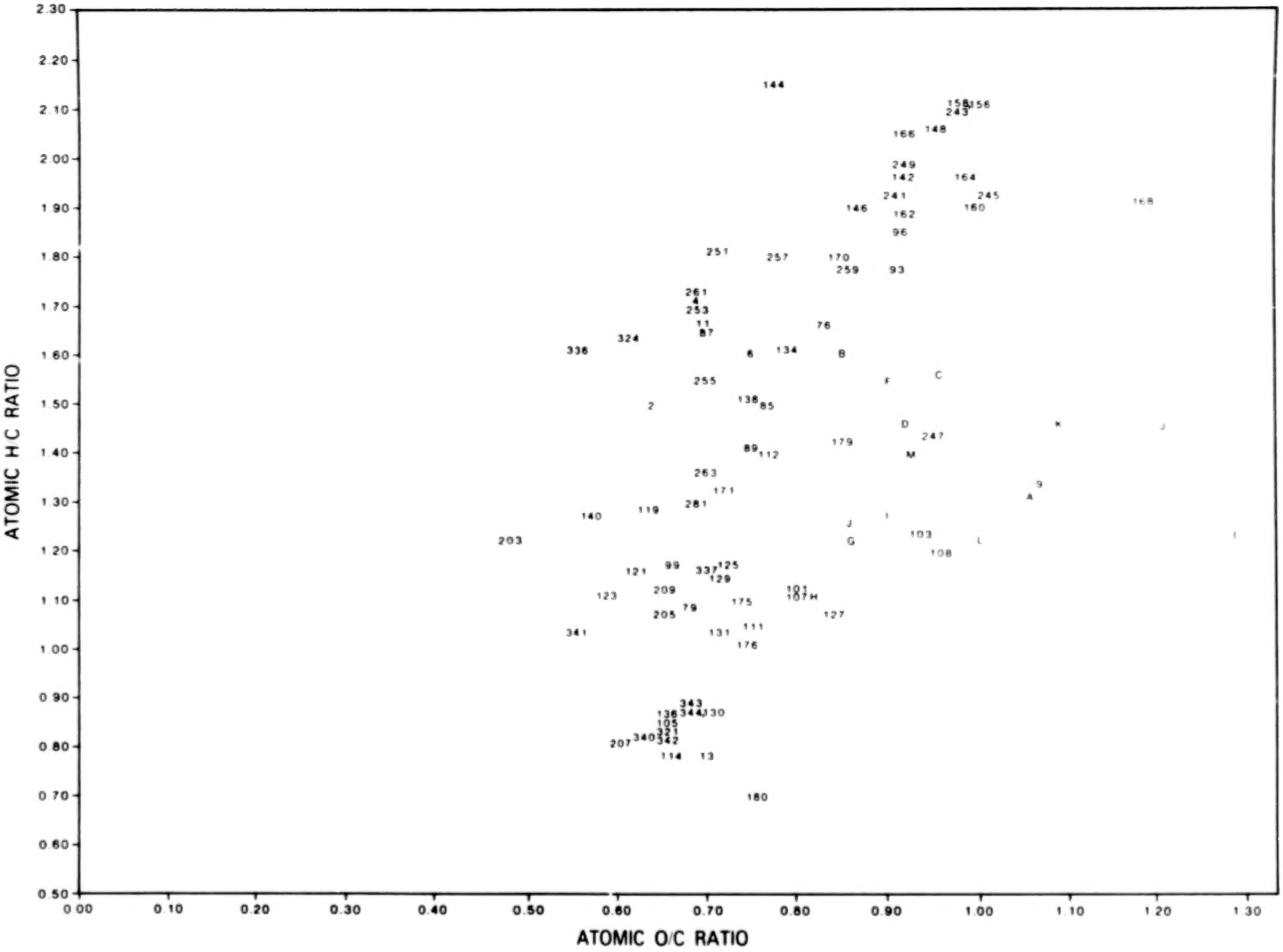

Figure 2.—Atomic H/C and O/C ratios of fulvic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

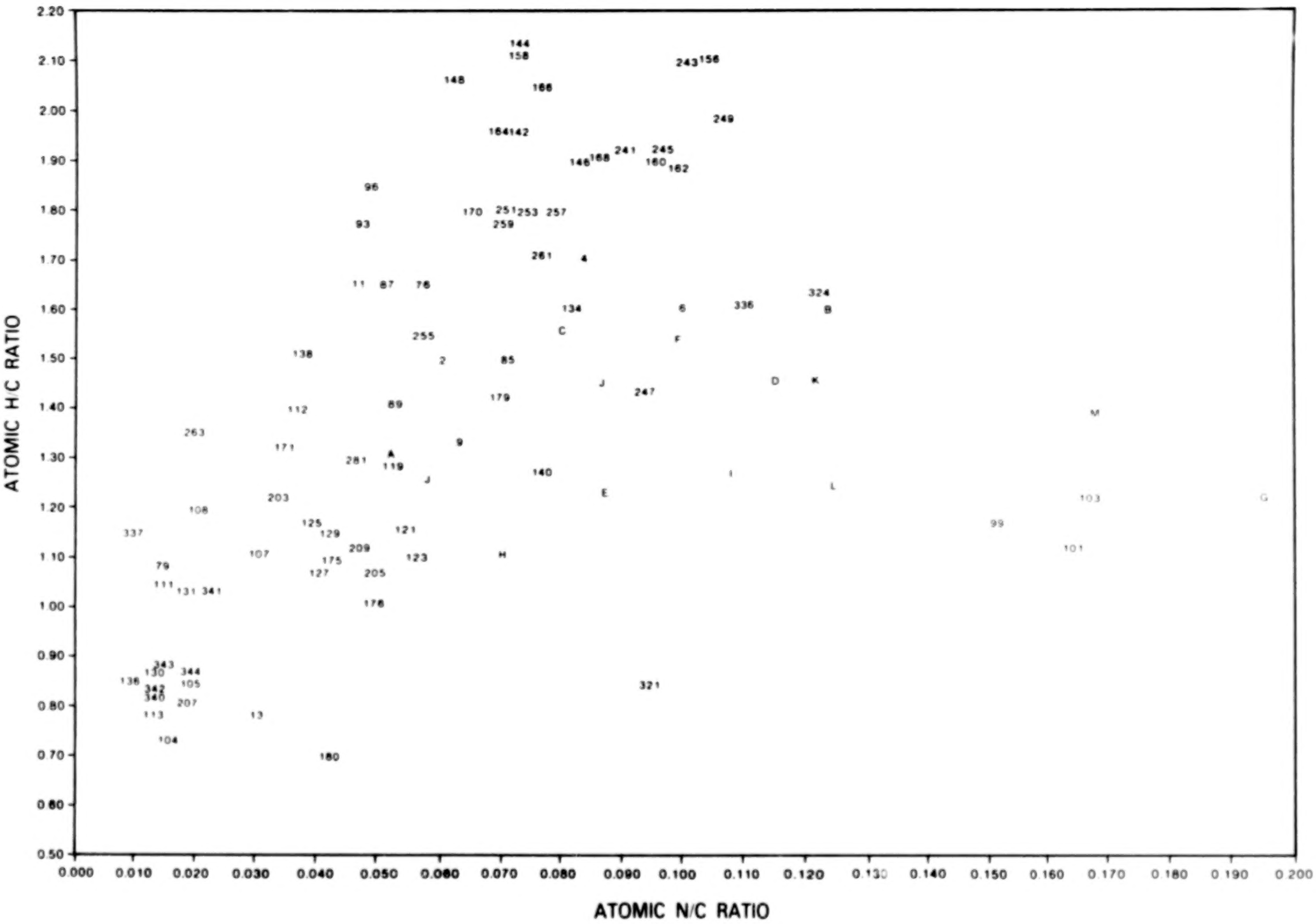

Figure 3.--Atomic H/C and N/C ratios of fulvic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

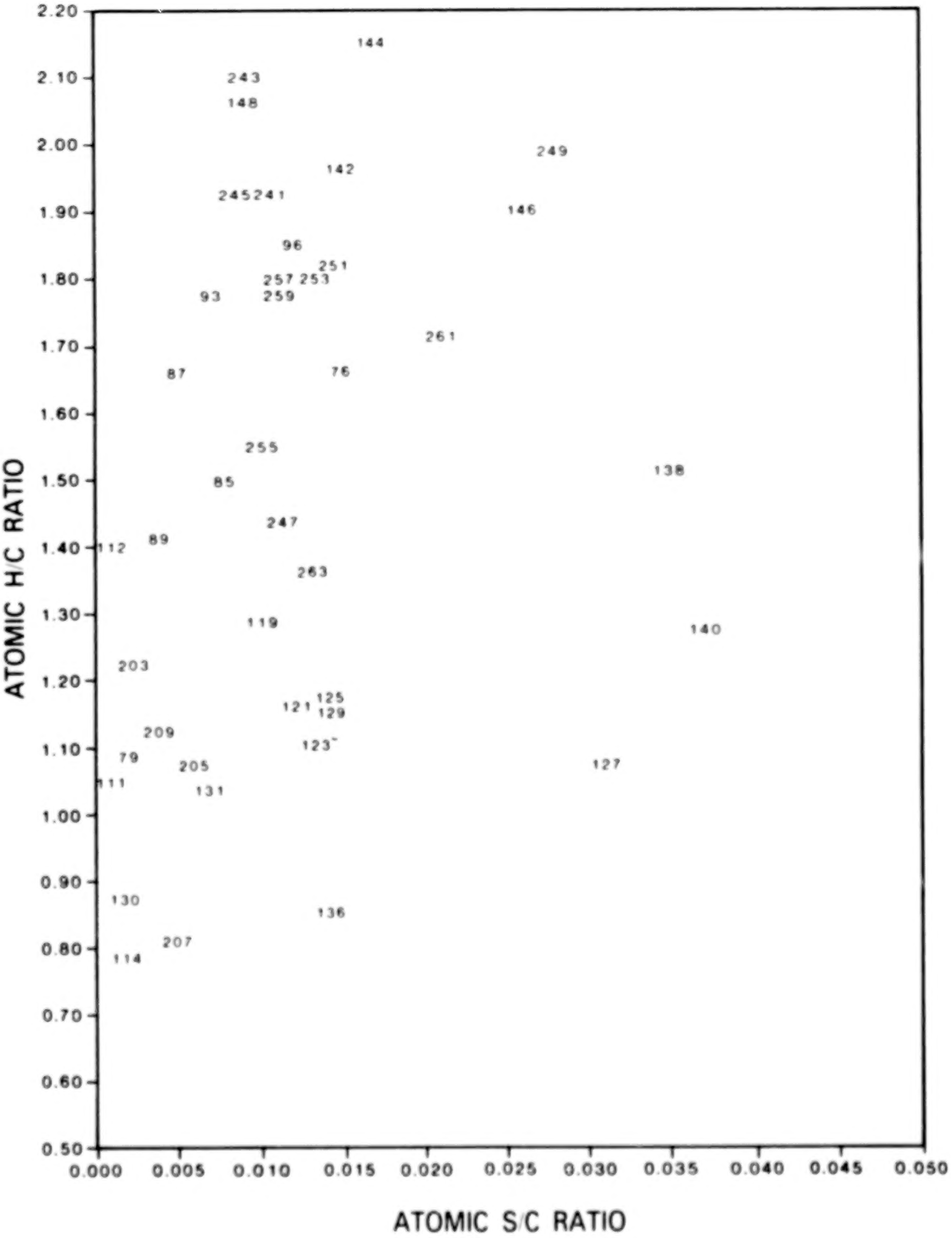

Figure 4.--Atomic H/C and S/C ratios of fulvic acids from soils and sediments. Numbers correspond to literature data in Appendix 1.

The elemental compositions of the humic acids isolated from the shelf and slope sediments in this study are presented in table 5 on a dry, ash-free basis. The carbon content of the humic acids ranged from 52.7 to 58.4 percent, hydrogen from 5.8 to 6.7 percent, nitrogen from about 5 to 6.9 percent, sulfur from 1.5 to 2.7 percent, and oxygen by difference ranged from 27.2 to 33.5 percent.

The composition of the humic acids isolated from the sediments from each of the geographical locations in this study area were quite similar, as indicated by the atomic ratios (table 5, figs. 5-7). The H/C ratios were relatively constant and ranged from 1.26 to 1.47. The atomic O/C ratios ranged from 0.35 to 0.48, the N/C from 0.073 to 0.108, and the S/C ratios from 0.010 to 0.019. By comparison with the literature data in appendix 1 and figures 5, 6, and 7, the humic acids in this study show atomic ratios similar to humic acids extracted from sediments in a number of locations, including the Black Sea (samples 28-31), the Saanich Inlet (samples 59-61), the Sea of Norway (samples 283-319) and the Bering Sea (samples 264-279), as well as several terrestrial soils (samples 23, 83, 141, 155, 161).

The elemental compositions of the protokerogens on a dry, ash-free basis are shown in table 6. The percent carbon of the protokerogens was found to range from 64.4 to 73.5 percent and the oxygen by difference ranged from 15.5 to 24.9 percent. Hydrogen, nitrogen, and sulfur percentages ranged from 4.5 to 8.6 percent, 1.8 to 4.2 percent, and 0.5 to 5.9 percent, respectively.

The atomic H/C ratios of the protokerogens showed a relatively wide range of 0.78 to 1.40 (table 6). The O/C atomic ratios ranged from 0.16 to 0.28, N/C from 0.021 to 0.054, and the S/C from 0.003 to 0.034. By comparison with the literature data in appendix 1 and figures 8, 9 and 10, the protokerogens in this study show atomic ratios similar to protokerogens isolated from marine sediments from the Black Sea (samples 211, 213, 219, 221, 223, 225, 227, 230,

Table 5 - Elemental composition and atomic ratios of humic acids isolated from Mid-Atlantic surface sediments by extraction with 0.5 N NaOH

			Elemental Composition, In Percent (Ash-free Basis)					Atomic Ratios			
Sample	Station	Ash Percent	%C	%H	%N	%S	%O*	H/C	O/C	N/C	S/C
A	A-2	5.8	58.27	6.35	4.96	2.05	28.37	1.30	0.37	0.073	0.013
B	B-1	8.3	57.88	6.41	6.32	2.18	27.21	1.32	0.35	0.094	0.014
C	C-4	9.1	54.24	6.39	4.96	2.72	31.69	1.40	0.44	0.078	0.019
D	D-4	8.1	54.59	6.74	6.88	--***	30.09	1.47	0.39	0.108	--
E	E-2	5.8	58.37	6.19	5.06	1.85	28.53	1.26	0.37	0.074	0.012
F	F-2	3.5	52.74	5.82	5.82	2.12	33.50	1.31	0.48	0.095	0.015
G	G-3	3.2	58.13	6.45	5.89	1.95	27.58	1.32	0.36	0.087	0.013
H	G-5	5.0	57.89	6.54	5.88	2.22	27.47	1.35	0.36	0.087	0.014
I	G-6	2.5	56.12	6.28	5.86	1.95	29.79	1.33	0.40	0.090	0.013
J	J-2	3.6	56.45	6.13	6.31	1.94	29.17	1.29	0.39	0.096	0.013
	J-2 #1**	6.0	54.78	6.01	6.84	1.95	30.42	1.31	0.42	0.107	0.013
K	K-4	2.4	55.44	6.23	6.12	1.95	30.26	1.34	0.41	0.095	0.013
L	K-5	2.9	56.20	6.34	5.34	1.54	30.58	1.34	0.41	0.081	0.010
M	K-6	4.8	57.19	6.14	5.22	1.96	29.49	1.28	0.39	0.078	0.013

*By difference.

**Method of extraction was by a combination of $NaOH-Na_4P_2O_7$.

***Sulfur was not determined due to analytical difficulties.

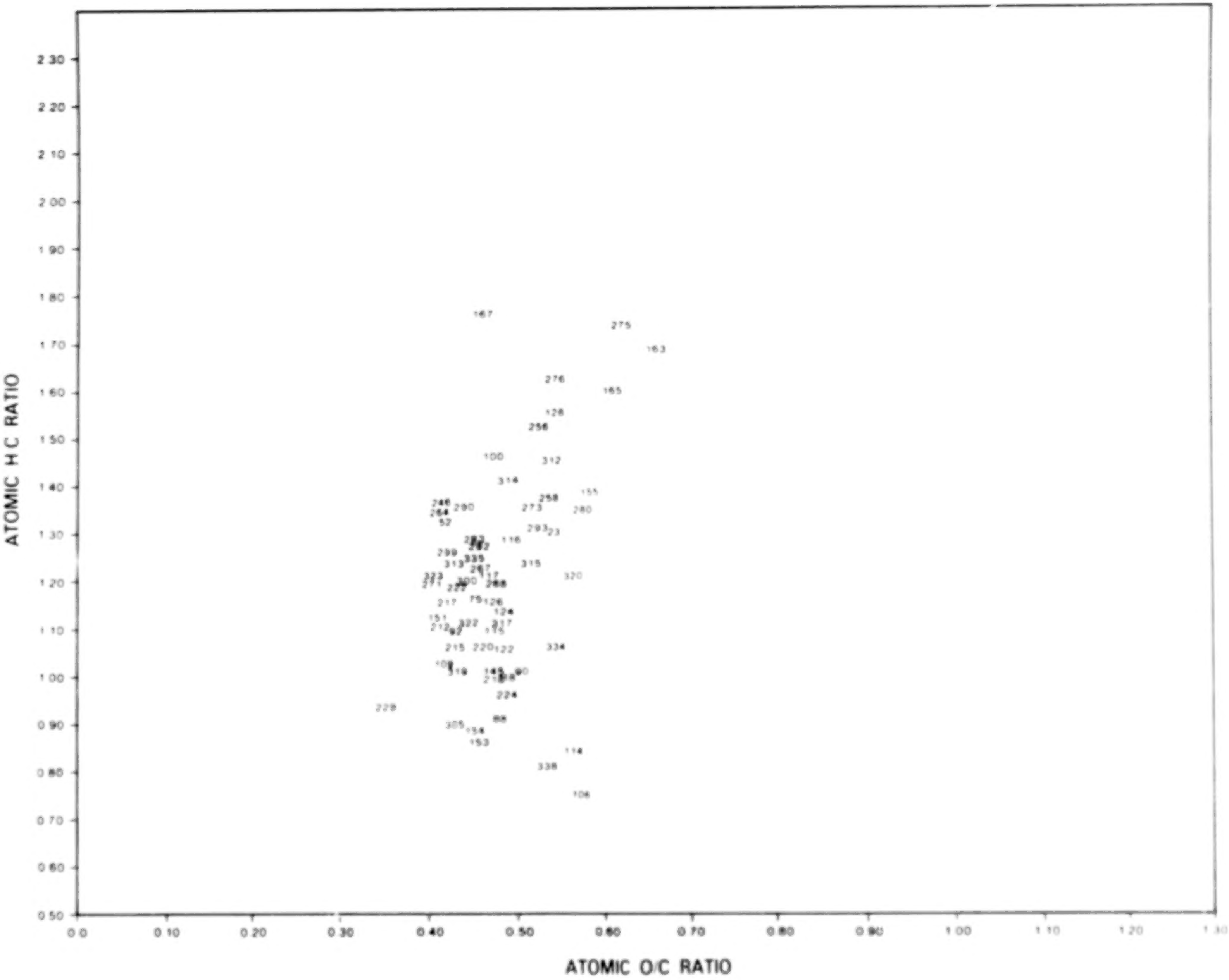

Figure 5.--Atomic H/C and O/C ratios of humic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

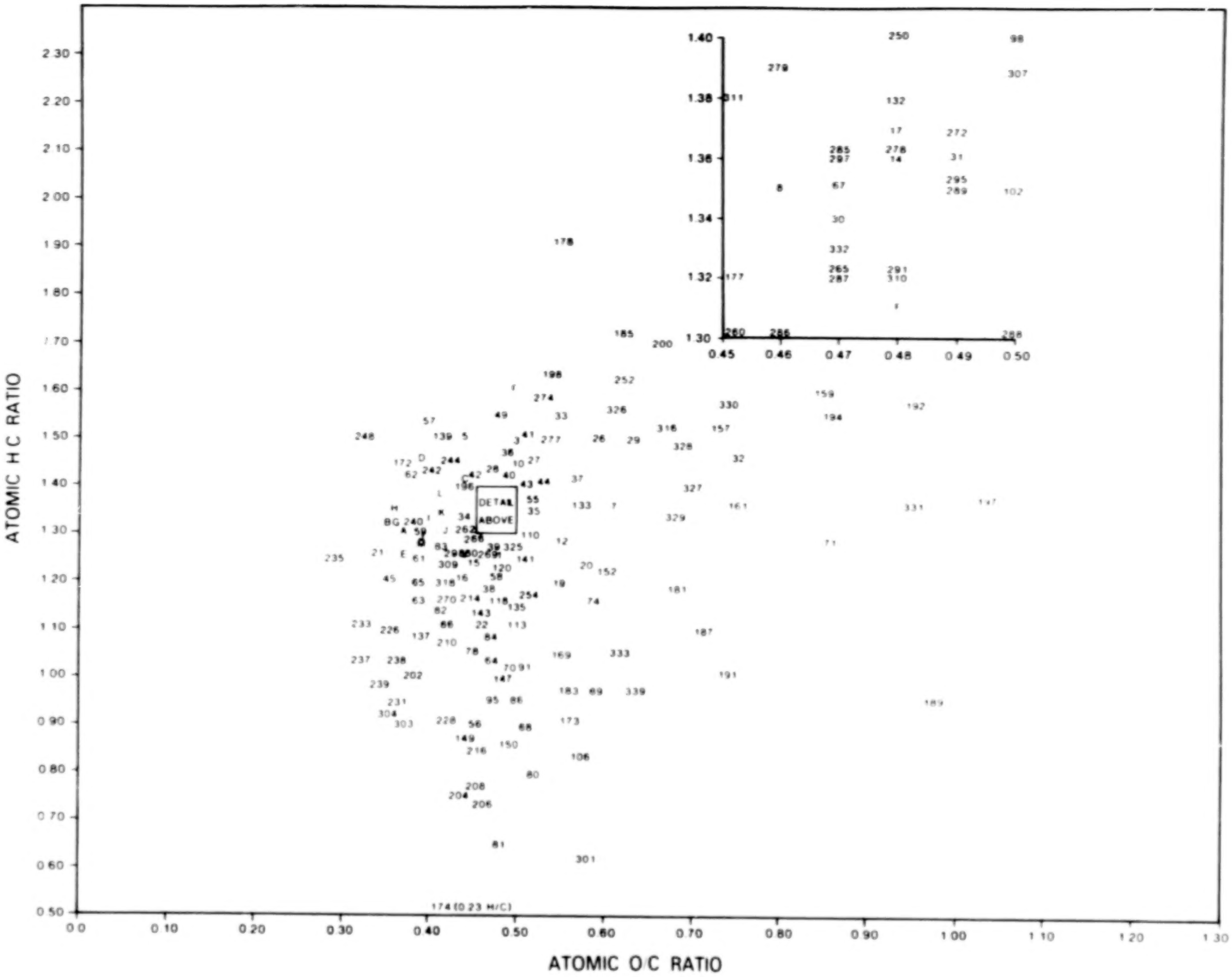

Figure 5.—Atomic H/C and O/C ratios of humic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study (continued).

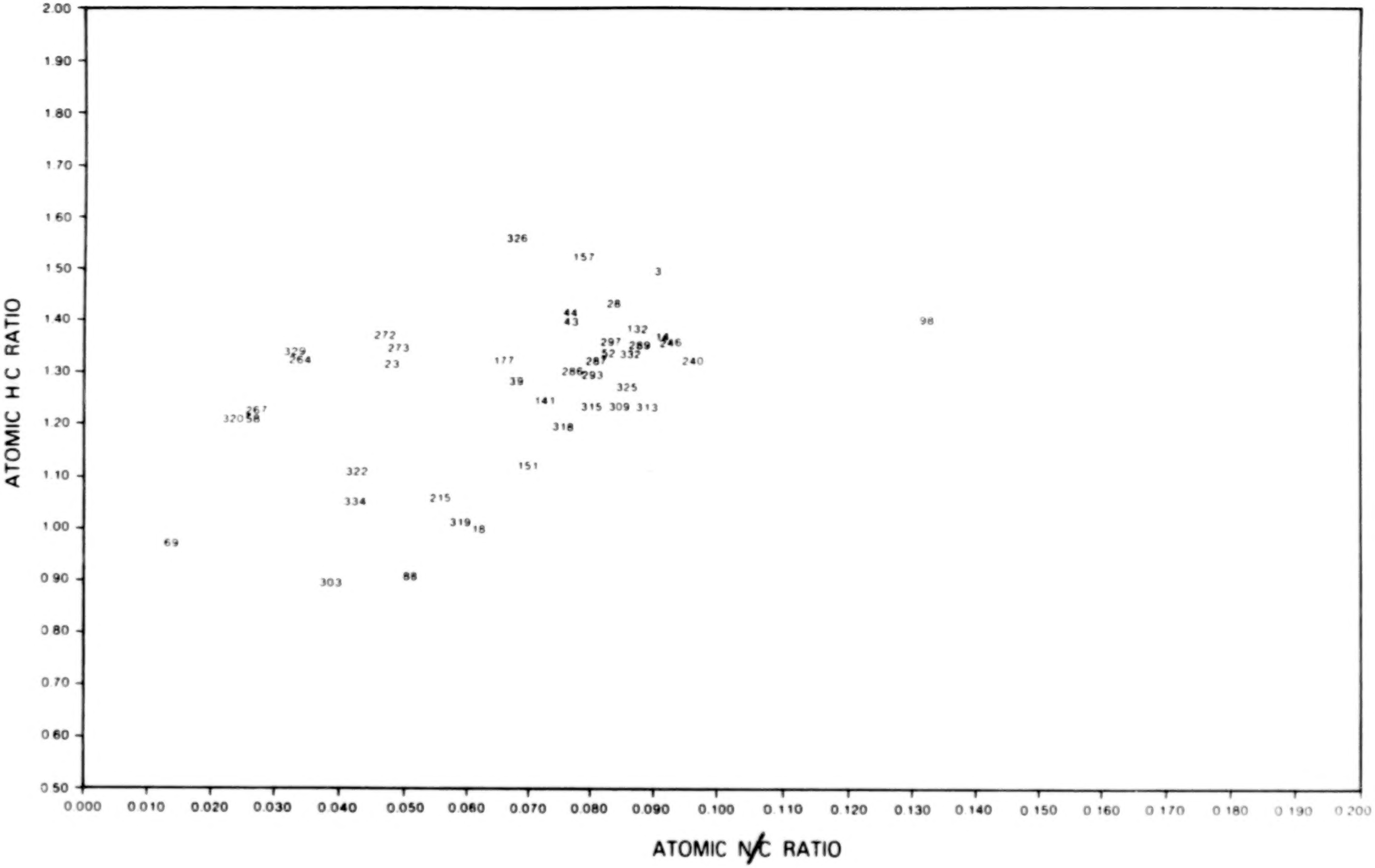

Figure 6.--Atomic H/C and N/C ratios of humic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

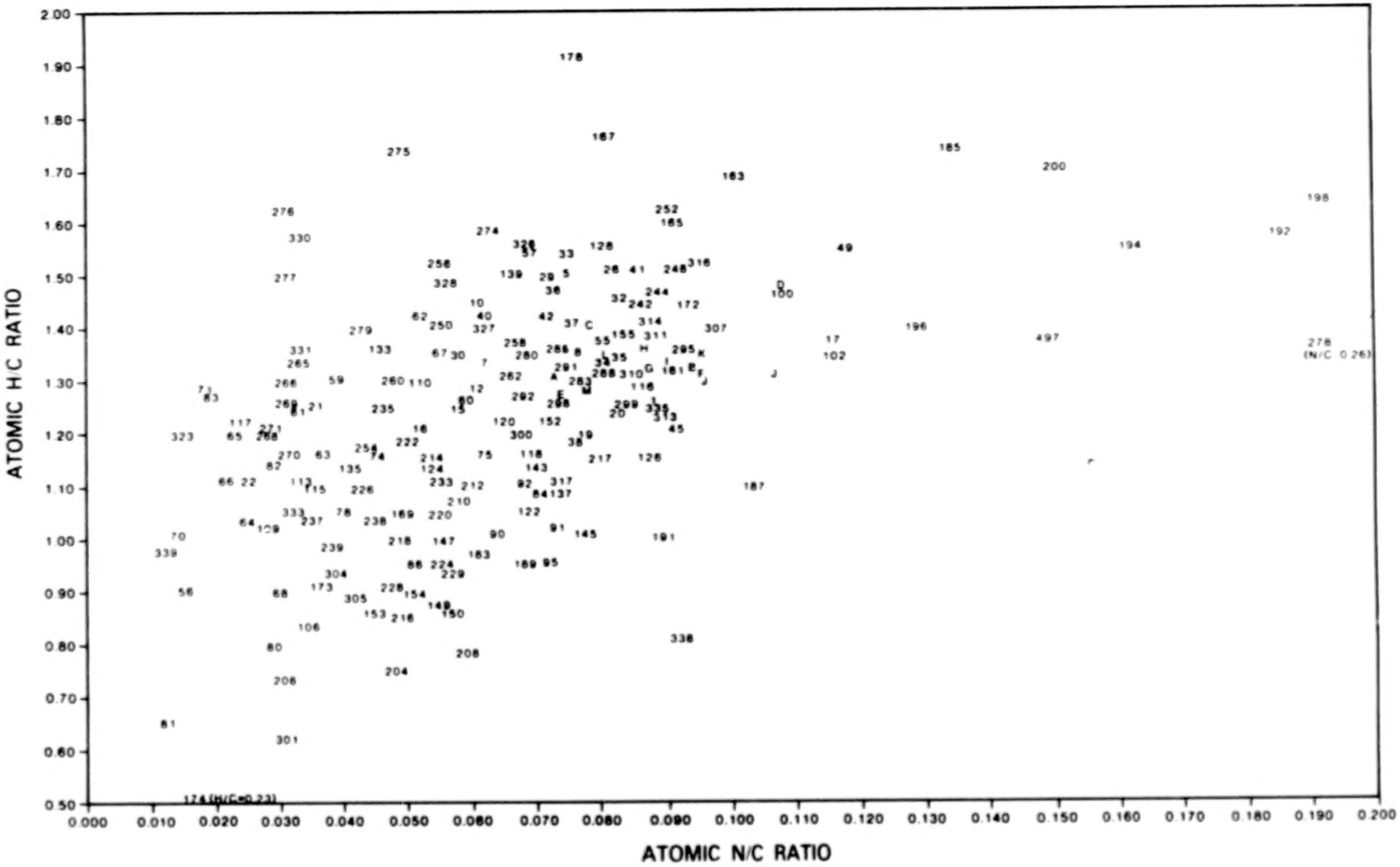

Figure 6.-- Atomic H/C and N/C ratios of humic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study (continued).

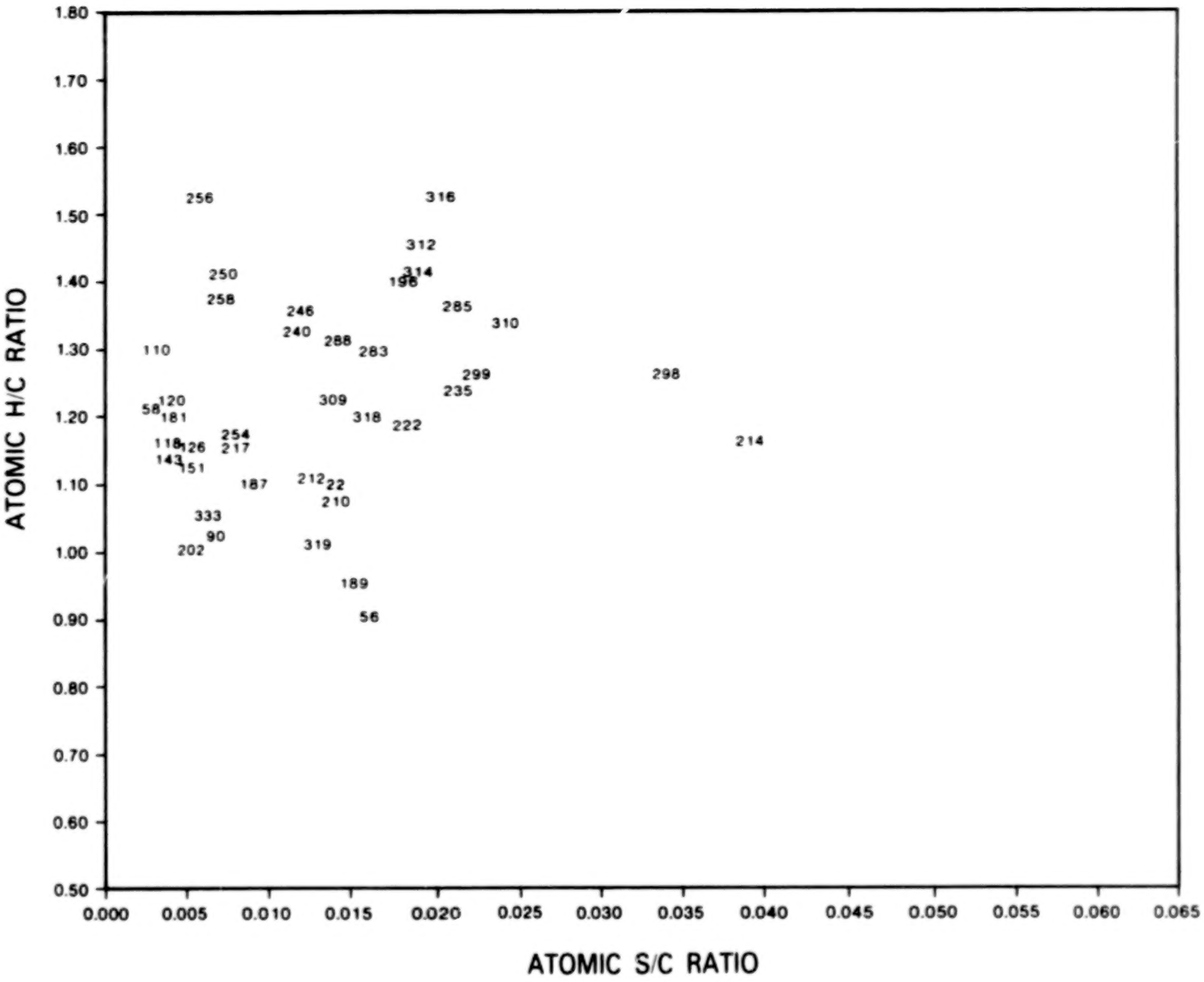

Figure 7.—Atomic H/C and S/C ratios of humic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

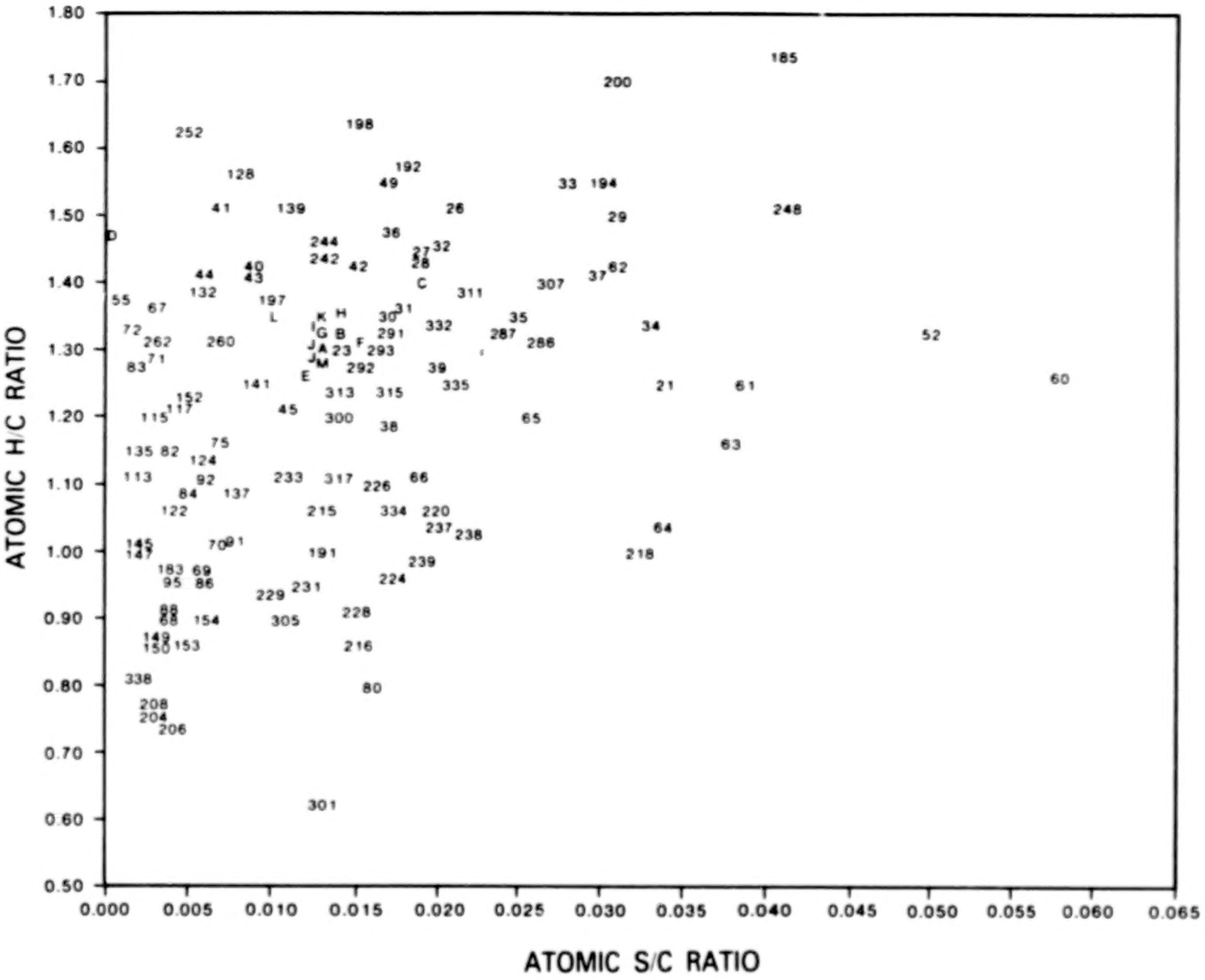

Figure 7.--Atomic H/C and S/C ratios of humic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study (continued).

Table 6 - Elemental composition and atomic ratios of protokerogen isolated from Mid-Atlantic surface sediments

			Elemental Composition, In Percent (Ash-free Basis)					Atomic Ratios			
Sample	Station	Ash Percent*	%C	%H	%N	%S	%O**	H/C	O/C	N/C	S/C
A	A-2	6.6	66.37	5.49	4.17	1.58	22.39	0.99	0.25	0.054	0.009
B	B-1	24.4	68.98	4.50	2.89	1.61	22.02	0.78	0.24	0.036	0.009
C	C-4	9.0	64.40	5.67	3.54	5.92	20.43	1.05	0.24	0.047	0.034
D	D-4	30.4	66.75	4.99	3.61	2.38	22.27	0.89	0.25	0.046	0.013
E	E-2	9.8	71.05	7.51	3.05	1.27	17.12	1.26	0.18	0.037	0.007
F	F-2	5.9	66.84	4.64	3.82	1.25	23.45	0.83	0.26	0.049	0.007
G	G-3	9.4	66.93	5.74	4.14	1.28	21.91	1.02	0.25	0.053	0.007
H	G-5	3.1	71.14	7.06	2.85	1.18	17.77	1.18	0.19	0.034	0.006
I	G-6	3.8	66.13	5.10	2.97	0.92	24.88	0.92	0.28	0.039	0.005
J	J-2	8.0	66.41	6.65	3.16	0.94	22.84	1.19	0.26	0.041	0.005
K	K-4	9.2	68.43	7.40	2.56	1.33	20.28	1.29	0.22	0.032	0.007
L	K-5	9.8	68.47	5.00	3.22	0.51	22.80	0.87	0.25	0.040	0.003
M	K-6	3.3	73.46	8.62	1.79	0.61	15.52	1.40	0.16	0.021	0.003

*Ash includes correction for loss in weight of FeS_2 converted to Fe_2O_3 during combustion.

**By difference.

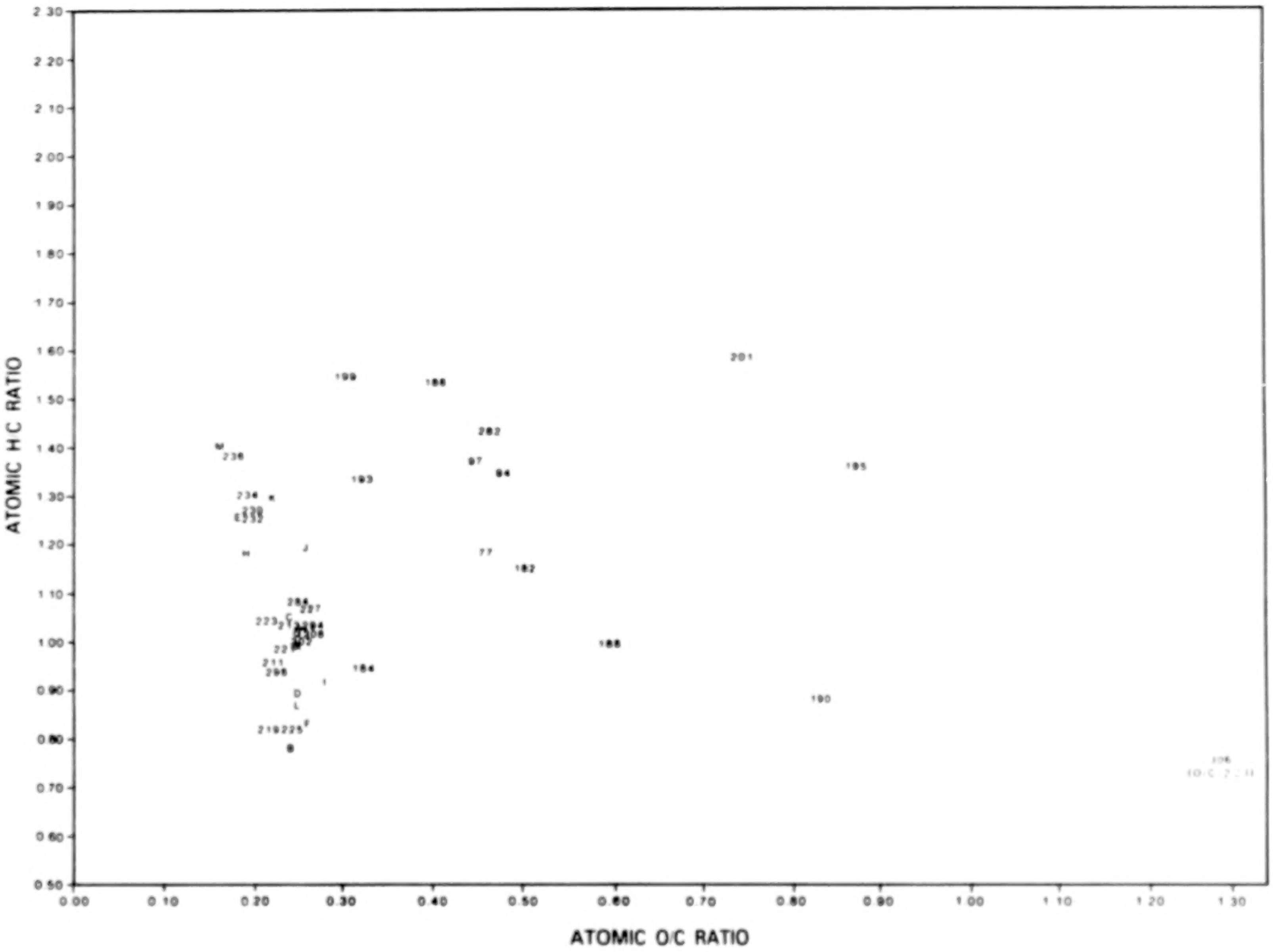

Figure 8.—Atomic H/C and O/C ratios of protokerogen from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

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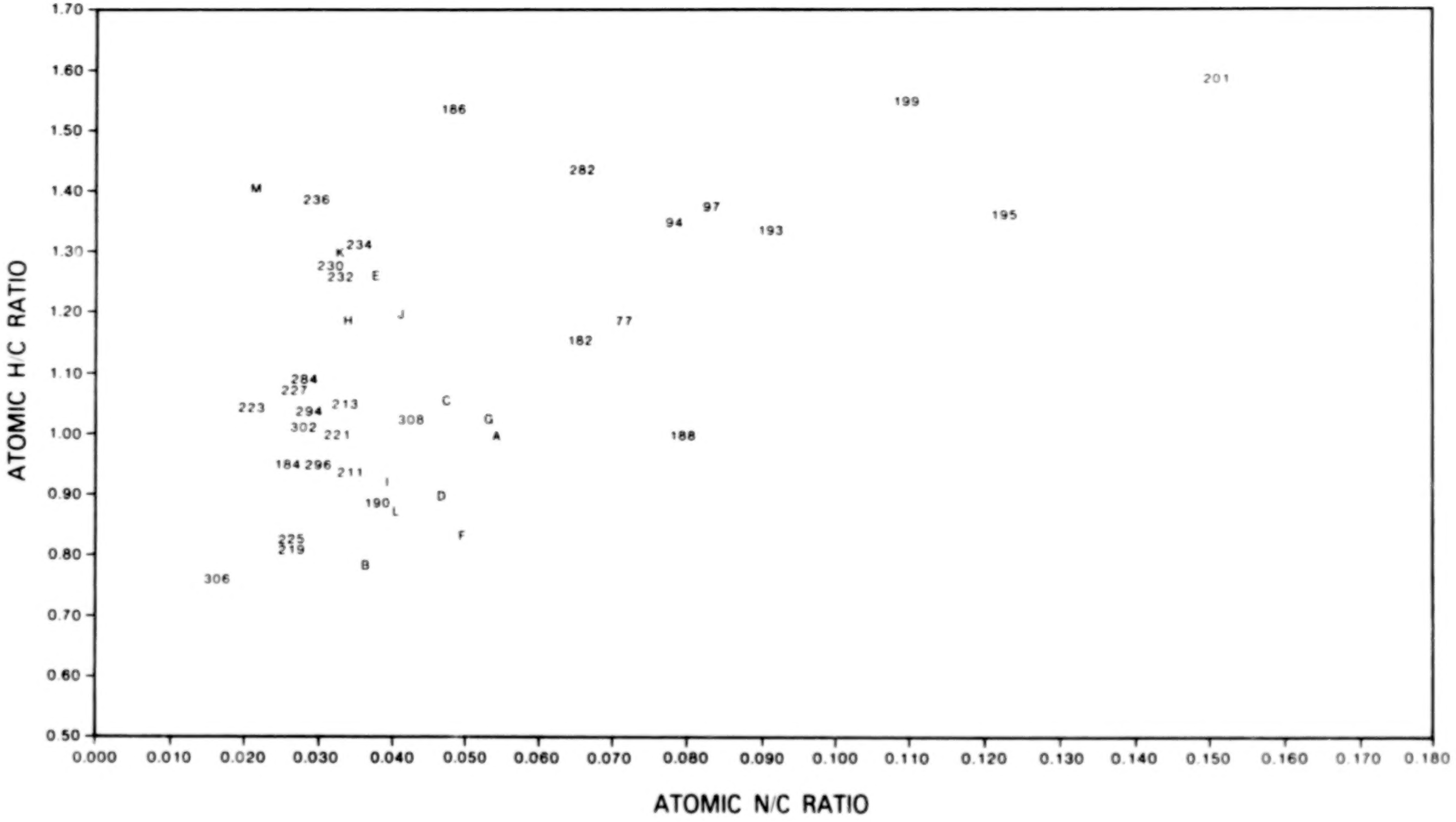

Figure 9.-- Atomic H/C and N/C ratios of protokerogen from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

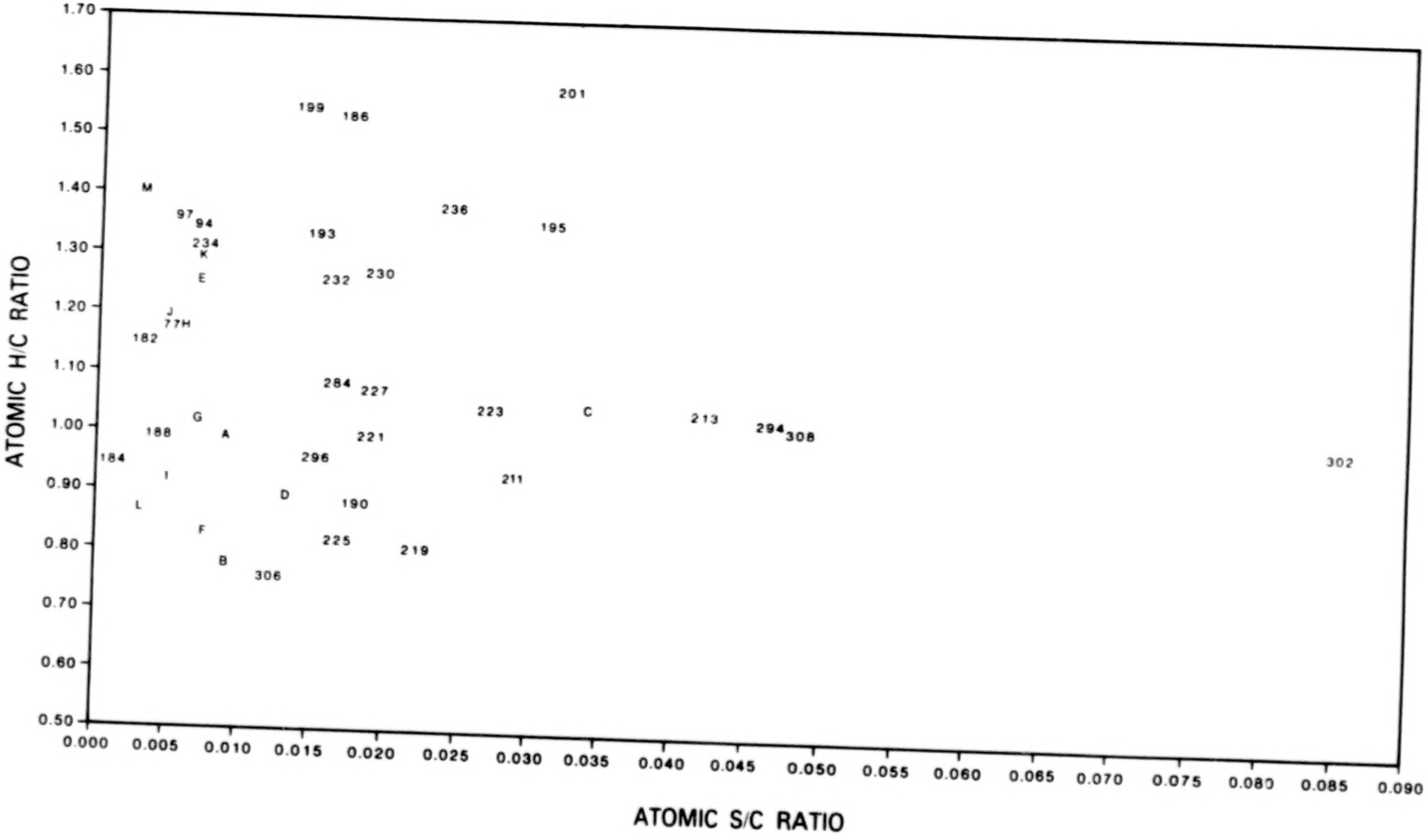

Figure 10.--Atomic H/C and S/C ratios of protokerogens from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

232, 234, 236), the Sea of Norway (samples 302, 306, 308), and the Tanner Basin (sample 193) as well as from soils from various locations (samples 77, 94, 97, 182).

The relatively wide range of the H/C ratios of the protokerogens contrasts with the relatively constant ratios determined for the humic acids isolated from the same sediments, which ranged from 1.26 to 1.47 (table 5). It is suggested that the relatively constant values of the atomic ratios of the humic acids are possible evidence of similar organic sources for the humic acids isolated from each of the shelf and slope sediments in this study. In contrast, the wider range of the atomic H/C ratios of the protokerogens may indicate a less homogeneous organic origin for the protokerogens, possibly as the result of input from reworked organic material which may include terrestrial organic matter.

Microscopic Examination

The protokerogen was viewed under transmitted and reflected light at magnifications of 250 and 400X. The major portion was observed to be dark brown or black in color and amorphous in character, although spores, pollen, wood cells, dinoflagellates, foraminifera, waxes, and algal cysts were also identified (E. Robbins, oral commun., 1981). Pollen were observed which were light yellow in color as opposed to the colorless appearance of recently deposited spores and pollen and were identified as of probable Late Cretaceous age (E. Robbins, oral commun., 1981).

Infrared Analyses

Infrared spectroscopy provides information on the functional groups present. Several factors, which include the structure and the concentration of the organic substance and the instrumental conditions of analysis such as scan time, speed of attenuator response, slit width, radiant power or amplifier gain, and balance, can affect the absorption intensity of functional groups in the analysis of organic compounds. The humic and fulvic acid concentrations and instrumental conditions were held constant in this study; thus variations in the spectra were apparently due mainly to the structural arrangement and functional groups. The same instrumental conditions were used for the protokerogens as for the fulvic and humic acids. Due to the darker color of the protokerogens compared to the fulvic and humic acids, however, it was necessary to use lower concentrations of the protokerogens to prepare KBr discs which were transparent. Although concentrations of the humic substances and the instrumental conditions may be different from those of published data, the similarity of the spectra in this study to spectra reported in the literature suggests that a comparison may be valid.

Each of the fulvic and humic acids in this study showed a broad, strong absorption band near 3400 cm^{-1}, which may be due to the absorption of hydrogen-bonded OH with a contribution from NH groups (figs. 11, 12). Absorption in this region was present, although greatly reduced, in the spectra of the protokerogens (fig. 13). Bellamy (1958) indicated that intermolecular hydrogen bonds of OH and NH groups in polymeric organic molecules give rise to broad absorption bands in the range of 3450 to 3200 cm^{-1}. Stevenson and Butler (1970), Stevenson and Goh (1971), and Debyser and others (1977b) attributed this band in the spectra of humic acids to hydrogen-bonded OH and NH groups, which include those of carboxylic acid and amide groups.

The sharp absorption bands near 2925 and 2850 cm^{-1} in the spectra of humic substances may be attributed to the CH stretching vibration of CH_2 and CH_3 in an aliphatic structure (Bellamy, 1958; Otsuki and Hanya, 1967; Goh and Stevenson, 1971; Debyser and others, 1977a). Humic acids that are

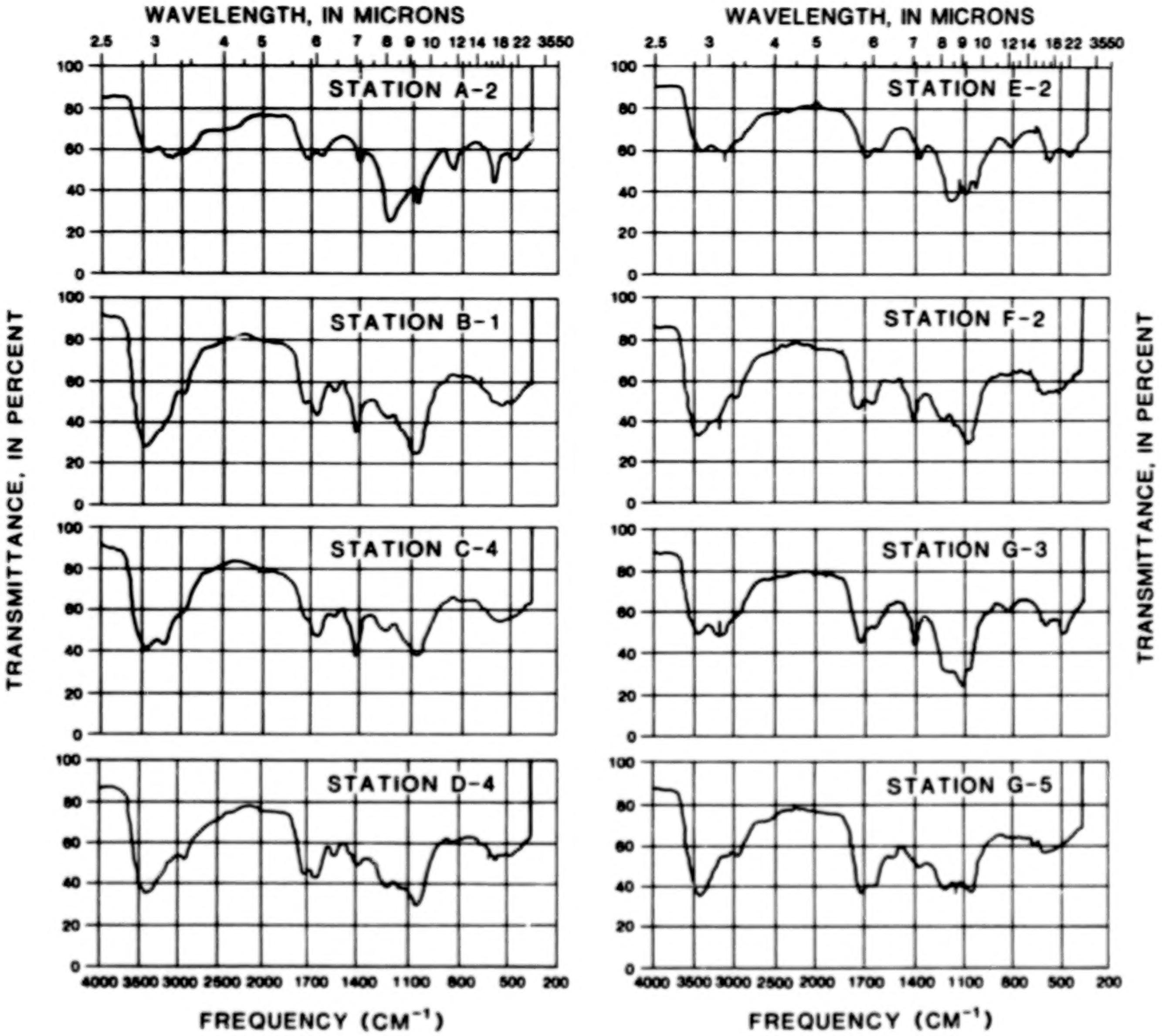

Figure 11.--Infrared spectra of humic acids isolated from Mid-Atlantic Shelf and Slope surface sediments.

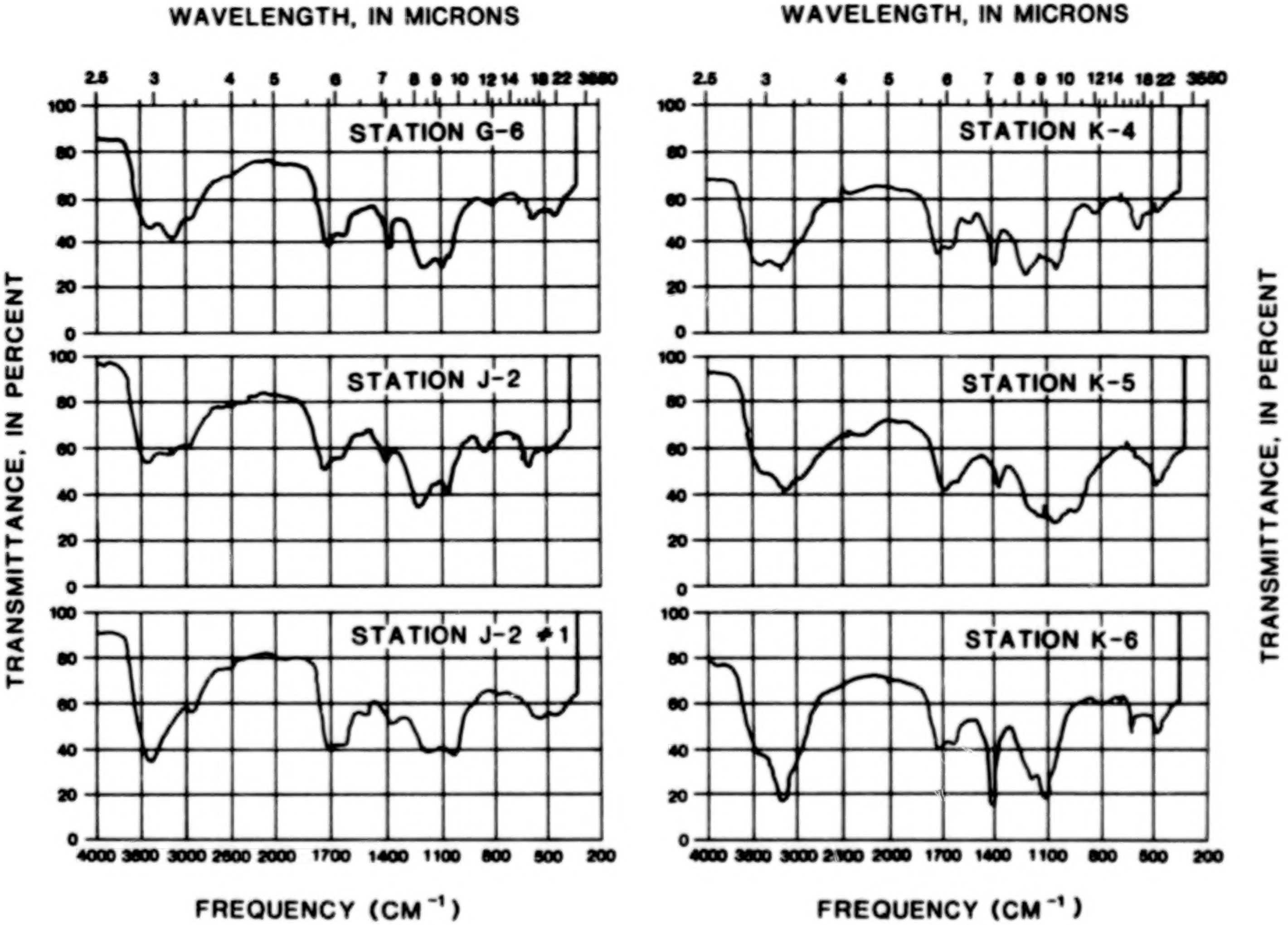

Figure 11.--Infrared spectra of humic acids isolated from Mid-Atlantic Shelf and Slope surface sediments (continued).

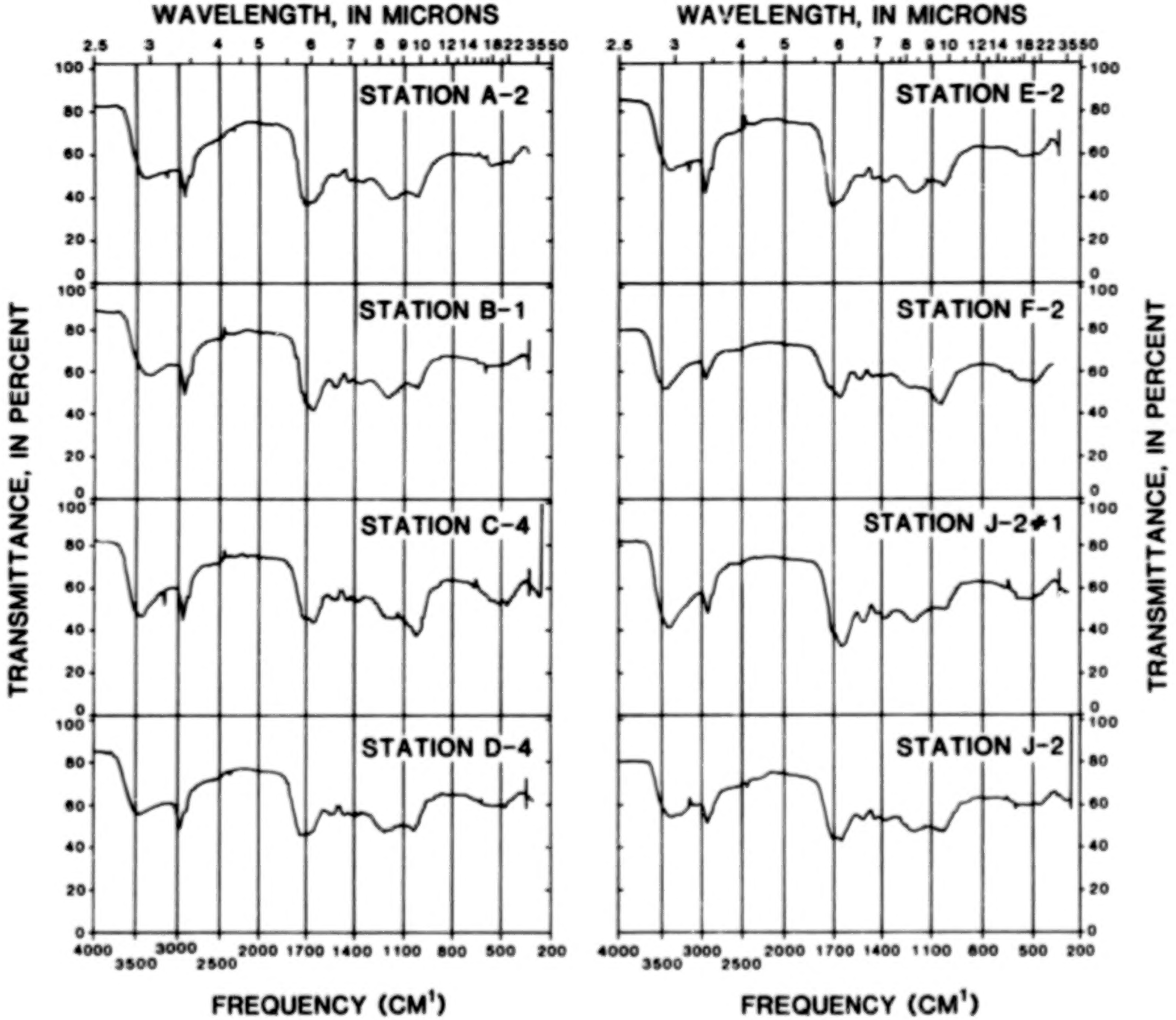

Figure 12.—Infrared spectra of fulvic acids isolated from Mid-Atlantic Shelf and Slope surface sediments.

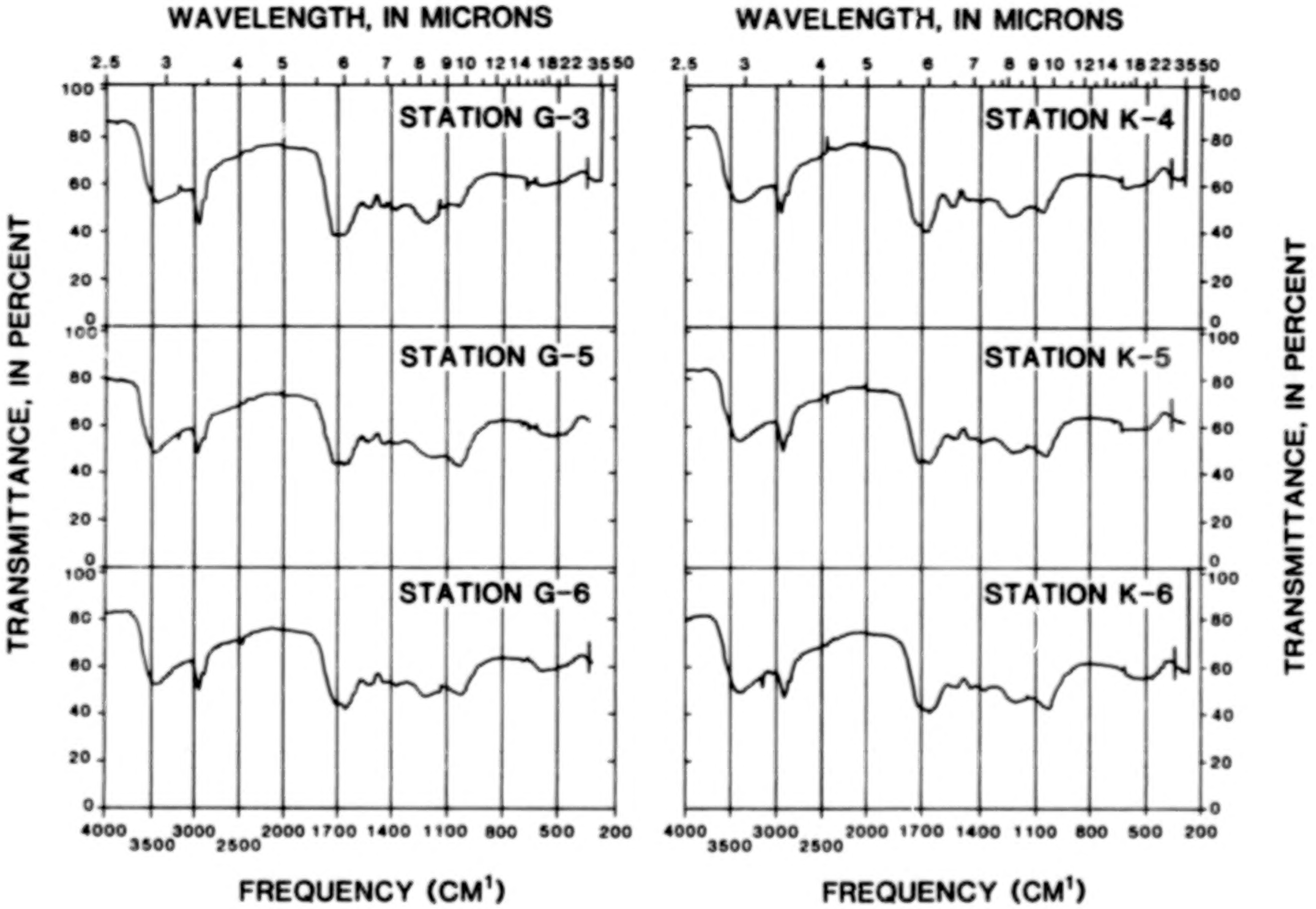

Figure 12.--Infrared spectra of fulvic acids isolated from Mid-Atlantic Shelf and Slope surface sediments (continued).

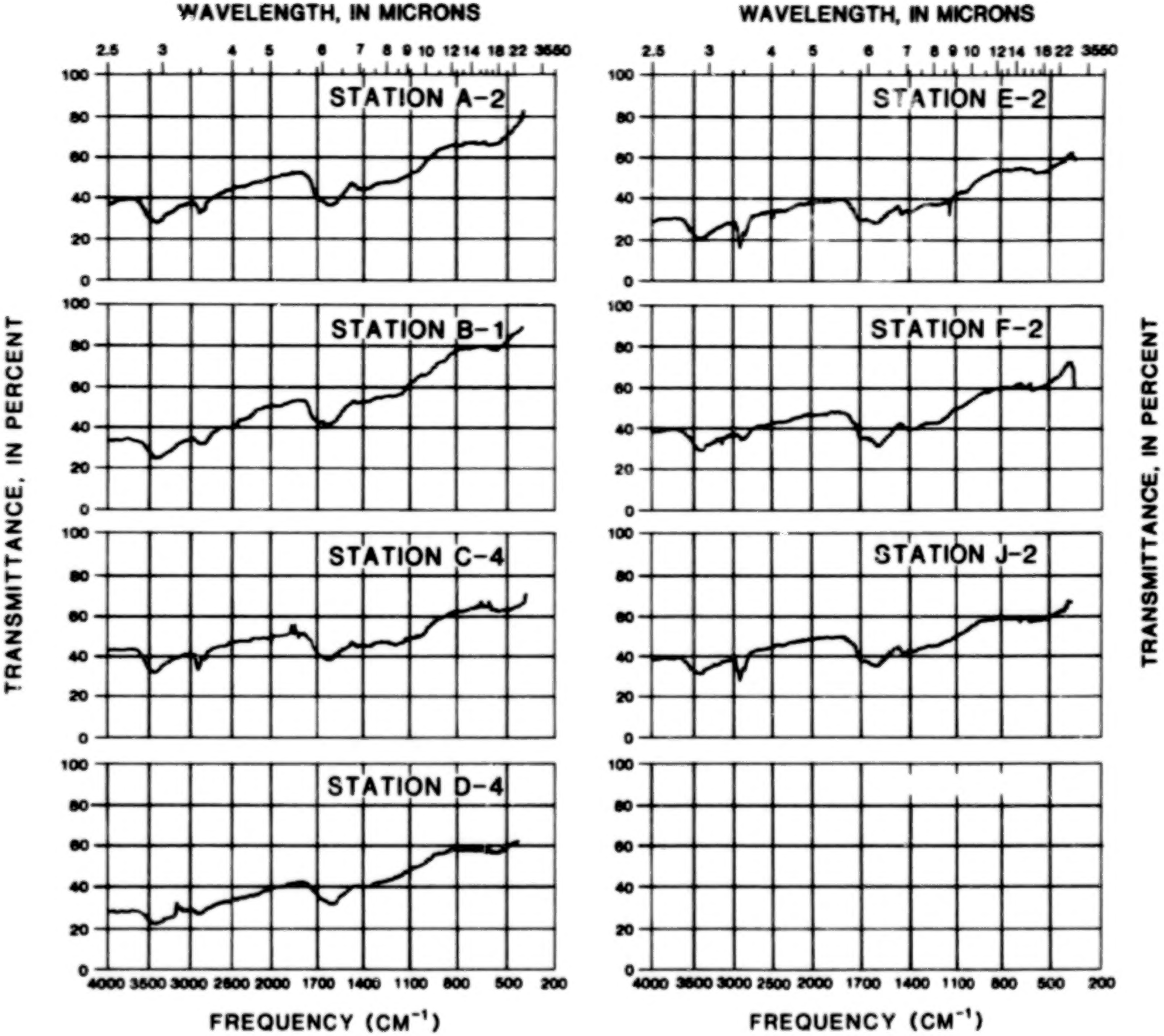

Figure 13.—Infrared spectra of protokerogens isolated from Mid-Atlantic Shelf and Slope surface sediments.

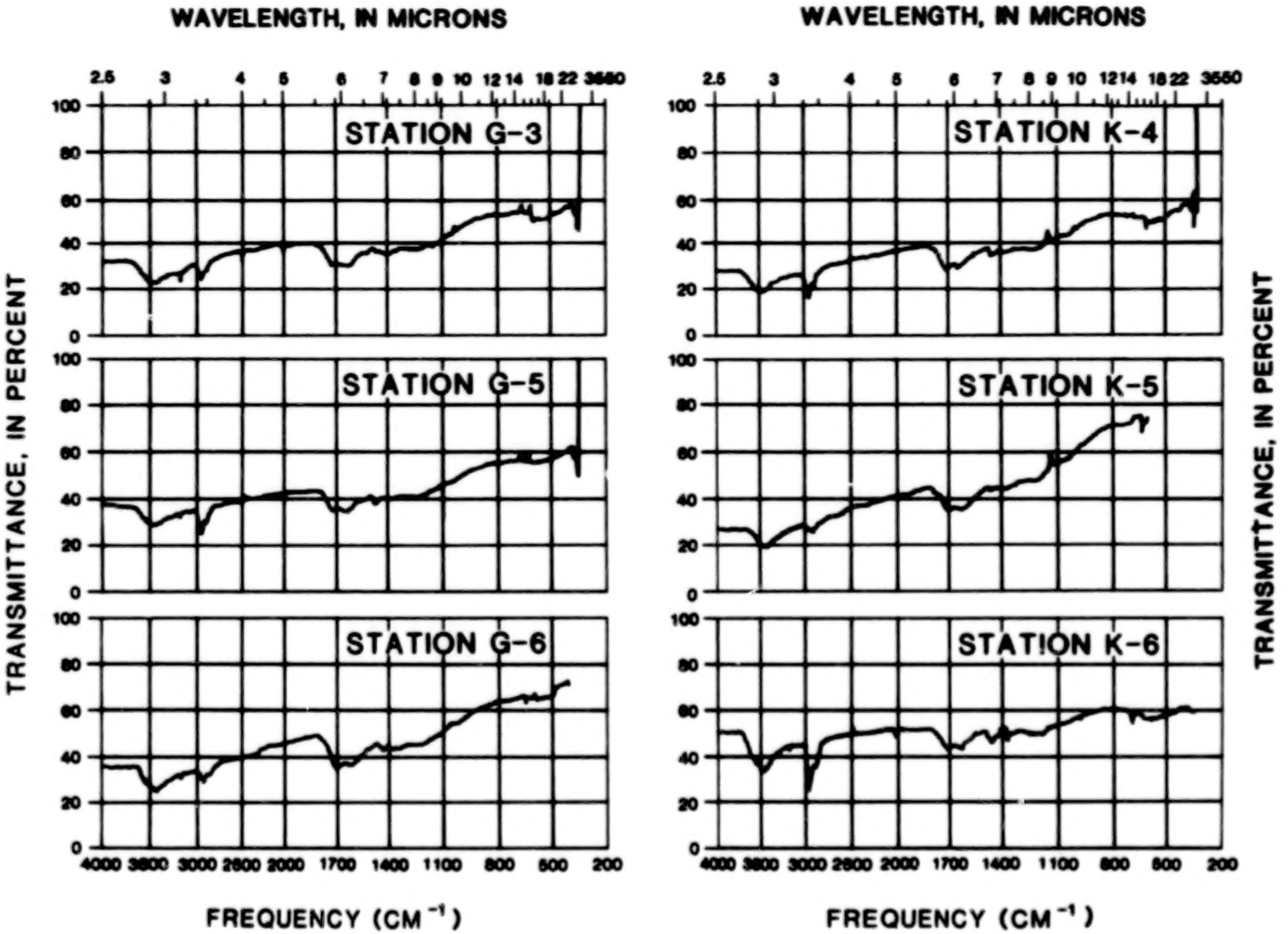

Figure 13.—Infrared spectra of protokerogens isolated from Mid-Atlantic Shelf and Slope surface sediments.(continued).

believed to be derived largely from terrestrial plant organic matter show weaker absorption intensity in the 2920-2850 cm^{-1} region relative to humic acids that are believed to be derived from organic matter with little terrestrial influence (Stevenson and Goh, 1971; Huc and others, 1975; Huc and Durand, 1977). In this study, absorption in the 2920-2850 cm^{-1} region for the fulvic acids is seen as a generally weak, poorly resolved shoulder on the side of the broad OH absorption band. In the spectra of the humic acids and protokerogens, this absorption is generally observed as relatively sharp bands in relation to other absorption bands in the spectra. Bellamy (1958) suggested that symmetrical and assymetrical bending occurs in the 1430-1470 and 1370-1380 cm^{-1} regions and weak bands near 1440 and 1370 cm^{-1} in the spectra of humic acids are tentatively attributed to CH_2 and CH_3 deformation (Otsuki and Hanya, 1967; Debyser and others, 1977a and b). In this study, these bands are very weak and poorly defined in the spectra of the protokerogens and are either absent or obscured by a sharp absorption band near 1410 cm^{-1} in the spectra of the fulvic acids.

Absorption bands near 1710 and 1200 cm^{-1} were present in the spectra of the fulvic and humic acids and protokerogens in this study. The reduced absorption in these regions in the spectra of the protokerogens may be due in part to the lower organic concentration in the KBr discs, 0.6 mg protokerogen compared to 0.8 mg fulvic and humic acids, and may also be due to the lower oxygen content of the protokerogens as compared to the fulvic and humic acids (approximately 20 percent oxygen in the protokerogens versus 51 percent and 30 percent oxygen in the fulvic and humic acids, respectively). The band near 1710 cm^{-1} in the spectra of humic and fulvic acids has been attributed to the C=O of carboxylic acids and carbonyl groups (Otsuki and Hanya, 1967; Huc and others, 1975; Debyser and others, 1977a and b).

Stevenson and Goh (1971) also observed that absorption near 1200 cm^{-1} in the spectra of humic acids bears a direct relationship to the intensity of the C=O stretching band near 1710 cm^{-1}, and attributed the absorption to C-O stretching and OH deformation of COOH groups.

Absorption in the 1660-1640 cm^{-1} region in the spectra of humic acids has been variously attributed to C=C vibrations of aromatic and conjugated systems, strongly hydrogen-bonded C=O of quinones, and hydrogen-bonded and conjugated ketones (Stevenson and Goh, 1971). In addition, bands in this spectral region are believed to be the result of the C=O stretching of amide I absorption in peptides (Otsuki and Hanya, 1967; Debyser and others, 1977a and b). Stevenson and Goh (1971) noted that in humic acids from lake sediments the band was greatly reduced in intensity by acid hydrolysis, and they suggested that this reduction may be evidence for peptide linkages. A rather weak band in the spectra of humic acids near 1540 cm^{-1} has been considered to possibly be due to NH bending vibrations of amide II absorption (Stevenson and Goh, 1971; Debyser and others, 1977a and b; Dereppe and others, 1980). The relatively high nitrogen content as evidenced by the atomic N/C ratios of the fulvic and humic acids in this study may support an interpretation of amide absorption for the bands near 1660 and 1540 cm^{-1} (table 2). The amide II absorption band near 1540 cm^{-1} is not apparent in the spectra of the protokerogens, which is consistent with the lower nitrogen and oxygen content of the protokerogens compared to the fulvic and humic acids and suggests that a loss of amide groups may have occurred in the formation of the protokerogens. In addition, absorption in the 1660 cm^{-1} region is shifted to slightly lower wavenumbers of 1620-1600 cm^{-1} in the spectra of the protokerogens. Rouxhet and others (1980) have suggested that a similar shift observed in their spectra of kerogens may be the result of a loss of oxygenated functional groups.

The spectra of the fulvic acids also included a very sharp absorption band near 1410 cm^{-1} (fig. 12). Stevenson and Goh (1971) noted that bands near 1400 and 1575 cm^{-1} appeared in their spectra when fulvic acids were converted to the salt forms and Schnitzer and Hoffman (1967) showed similar absorption bands for fulvic acid salts and complexes with a series of metals. Although this specific absorption band may suggest that a portion of the oxygen-containing functional groups in the fulvic acids examined in this study may be associated with metals, the band near 1575 cm^{-1} noted by Schnitzer and Hoffman (1967) was absent.

Stable Carbon Isotope Analyses

Stable carbon isotopic compositions were determined on the humic and fulvic acids and protokerogens isolated from stations A-2, D-4, J-2, and K-5, and on the humic acid from station F-2 sediments (table 7). The $\delta^{13}C$ isotopic ratios of the humic acids were fairly constant and varied by 2.1 per mil, from -21.2 to -23.3 per mil, with an average of -22.4 per mil. The relatively constant $\delta^{13}C$ ratios are consistent with the elemental compositions and infrared spectra interpretations for each of the humic acids, and support the notion of a similar source and structure for the humic acids from each of these sediments. The variation in the carbon isotopic ratios of the fulvic acids was 2.3 per mil, similar to that of the humic acids, and ranged from -21.5 to -23.8 per mil with an average of -22.5 per mil. The $\delta^{13}C$ ratios of the protokerogens were very consistent and ranged from -25.0 to -25.4 per mil.

The $\delta^{13}C$ isotopic ratios of common terrestrial plants typically range from about -22 to -31 per mil, with a mean value of approximately -26 per mil, whereas marine plankton are isotopically heavier with ratios that range from about -18 to -24 per mil and show a mean of about -21 per mil (Degens, 1969).

Table 7 - Stable carbon isotopic composition of humic acid, fulvic acid and protokerogen isolated from Mid-Atlantic surface sediments

Sample	Station	^{13}C* Fulvic Acid (per mil)	^{13}C* Humic Acid (per mil)	^{13}C* Protokerogen (per mil)
A	A-2	-23.8	-22.4	-25.0
D	D-4	-22.1	-23.3	-25.2
F	F-2	--**	-21.2	--**
J	J-2	-21.5	-22.8	-25.4
L	K-5	--***	-21.9	-25.0

*Relative to the PDB standard. Precision is estimated to be ± 0.02 permil.

**Not determined.

***CO_2 sample lost prior to isotopic analysis.

Comparison of the humic acid data in figure 14 with appendix 1 shows that the majority of humic acids with an atomic H/C ratio of greater than 1.20 and a $\delta^{13}C$ ratio heavier than -23 per mil were extracted from sediment that was believed to contain predominantly marine organic matter. Protokerogen isolated from sediments and soils with a predominantly terrestrial organic matter input had $\delta^{13}C$ ratios lighter than -27 per mil and generally had H/C ratios less than 1.20 (fig. 15). The average $\delta^{13}C$ ratio of the humic and fulvic acids in this study, -22.4 per mil, was 1.4 per mil lighter than the mean value for marine plankton given by Degens (1969), yet was 3.6 per mil heavier than the mean $\delta^{13}C$ ratio of common terrestrial plants. The $\delta^{13}C$ isotopic ratios of the protokerogens, however, were only about 1 per mil heavier than the mean value for common terrestrial plants. The $\delta^{13}C$ ratios of the protokerogens were between 1.2 and 3.9 per mil lighter than the fulvic and humic acids in the samples from each of the four stations analyzed. Several explanations can be proposed for the isotopic differences:

(1) The humic and fulvic acids may not be derived from an entirely marine source of organic carbon but may include trace inputs from terrestrial sources. The influx of terrestrial organic matter to the lipoidal fraction which is suggested by the hydrocarbon analyses reported by Miller and others (1979a) may also have influenced the formation of the humic substances and their isotopic ratios. The addition of organic matter derived from terrestrial plants would decrease the $\delta^{13}C$ ratio of the humic substances and result in a ratio isotopically lighter than marine plankton.

(2) The isotopic ratios of the humic and fulvic acids may reflect the isotopic composition of the marine plankton from this region. Sackett and others (1965) and Degens and others (1968) have shown that the $\delta^{13}C$ ratio of plankton are influenced by water temperature. Also, plankton from colder

regions are isotopically lighter than those from tropical waters. The $\delta^{13}C$ ratios reported by Degens (1969) are for plankton at 22°C. The water temperatures on the Mid-Atlantic Shelf, however, are estimated to be somewhat lower, ranging between 4 and 20°C based on the temperature-depth profiles published by Ruzecki and others (1977). The planktonic $\delta^{13}C$ ratio may, therefore, be expected to be in the isotopically light end of the range given by Degens (1969), although the $\delta^{13}C$ ratios of plankton in this region have apparently not been reported.

(3) It has been proposed that alteration of the progenitor source organic matter during formation of the humic and fulvic acids may result in an isotopic fractionation of the organic carbon with a preferential loss of ^{13}C (Nissenbaum and Kaplan, 1972; Steurmer and others, 1978; Galimov, 1980). In this study, the protokerogens contained higher carbon and hydrogen as well as lower oxygen and nitrogen contents than the fulvic and humic acids from the same sample. In addition, the atomic ratios were also generally lower in protokerogen than those of the fulvic and humic acids. The intensity of the absorptions of oxygen-containing functional groups in the 3400, 1710, 1660, and 1540 cm^{-1} wavelength regions in the infrared spectra was weakest in the protokerogens, slightly greater in the humic acids, and strongest in the fulvic acids, which followed the same trend as the elemental oxygen and nitrogen compositions. The lower oxygen and nitrogen contents and higher carbon content of the protokerogens compared to the fulvic and humic acids may support the interpretation that a loss of oxygen- and nitrogen-containing functional groups may have occurred during the formation of protokerogen. Carbon-oxygen functional groups are believed to become enriched in the ^{13}C isotope compared to the molecule as a whole as a result of fractionation during biosynthesis (Galimov, 1974, 1980). Continued condensation and

polymerization of the organic matter may also reduce the $\delta^{13}C$ ratio of the residue (Galimov, 1980).

(4) The lighter $\delta^{13}C$ isotopic ratios of protokerogen relative to fulvic and humic acids may suggest that the protokerogen consists of mixtures of reworked and primary organic matter. A portion of protokerogen in sediments may be of detrital origin, reworked from a previous deposit and transported to the shelf sediments (Sackett and others, 1974; Tissot and Welte, 1978). Reworked organic matter may also be incorporated into the surface sediments in this region as a result of mixing from older sediments underlying the surficial sands. Knebel and Spiker (1977) concluded that surficial sand sheets in the Baltimore Canyon Trough area generally show radiocarbon age dates of less than 10,000 years B.P. and are probably of Holocene age. The underlying muddy unit had radiocarbon age dates of greater than 24,000 years B.P. and is believed to be Pleistocene in age. In an area of a thin sand layer, an age of greater than 40,000 years was determined for the surface sediments and attributed to older shells mixed with younger sediments through processes that may have included waves, tidal currents, benthic organisms, wind-derived currents, internal waves, and canyon-related currents (Knebel and Folger, 1976). The light yellow-colored pollen of probable Late Cretaceous age present in the protokerogen indicate an input of reworked organic matter which has undergone a previous thermal history.

Durand and Nicaise (1980) have suggested that a large part of the organic residue from the acid demineralization probably consists of reworked organic matter, which is believed to be more resistant to acid hydrolysis than more recently formed organic matter. In this present study, the organic matter, which is insoluble in the alkaline extraction, is believed to be susceptible to acid attack, as shown by the average hydrolyzable fraction of 40 percent.

This may suggest that O- and N-containing functional groups were present and were preferentially removed as a portion of the hydrolyzable fraction. The O-containing functional groups are believed to contain a greater proportion of the ^{13}C isotope compared to the molecule as a whole (Galimov, 1980). The insoluble residue, therefore, might be expected to be lower in O- and N-containing functional groups and in the ^{13}C isotope compared to the hydrolyzable fraction.

(5) Miller and others (1979a) noted the presence of traces of coal in some of the Mid-Atlantic surface sediments, and Degens (1969) reported that coals generally have $\delta^{13}C$ isotopic ratios of -23 to -25 per mil. In this study, traces of coal were also observed in the sediment samples from stations C-4 and D-4, but were apparently absent in the other sediment samples. It is believed that the coal probably would not represent a large percentage of the organic carbon in the sediment, and the influence of coal on the $\delta^{13}C$ isotopic ratios is believed to be slight.

The atomic H/C and $\delta^{13}C$ isotopic ratios of the fulvic and humic acids and protokerogens isolated in this study are included in figures 14, 15, and 16. Tissot and Welte (1978) have observed consistent differences in elemental compositions between kerogens of terrestrial and marine origins, with a more aliphatic character and hydrogen-rich nature in kerogen of marine origin. Huc and Durand (1977) extended these observations to humic acids of ancient sediments and found a direct relationship between the humic acids and kerogens of the same sample. They suggested that humic acids from marine sources show a higher H/C ratio and more prominent absorption bands in the infrared spectra assigned to CH aliphatic bonds (2920-2850 cm^{-1}) than humic acids derived from terrestrial organic matter. The relatively hydrogen-rich nature of the fulvic and humic acids in this study, as suggested by the

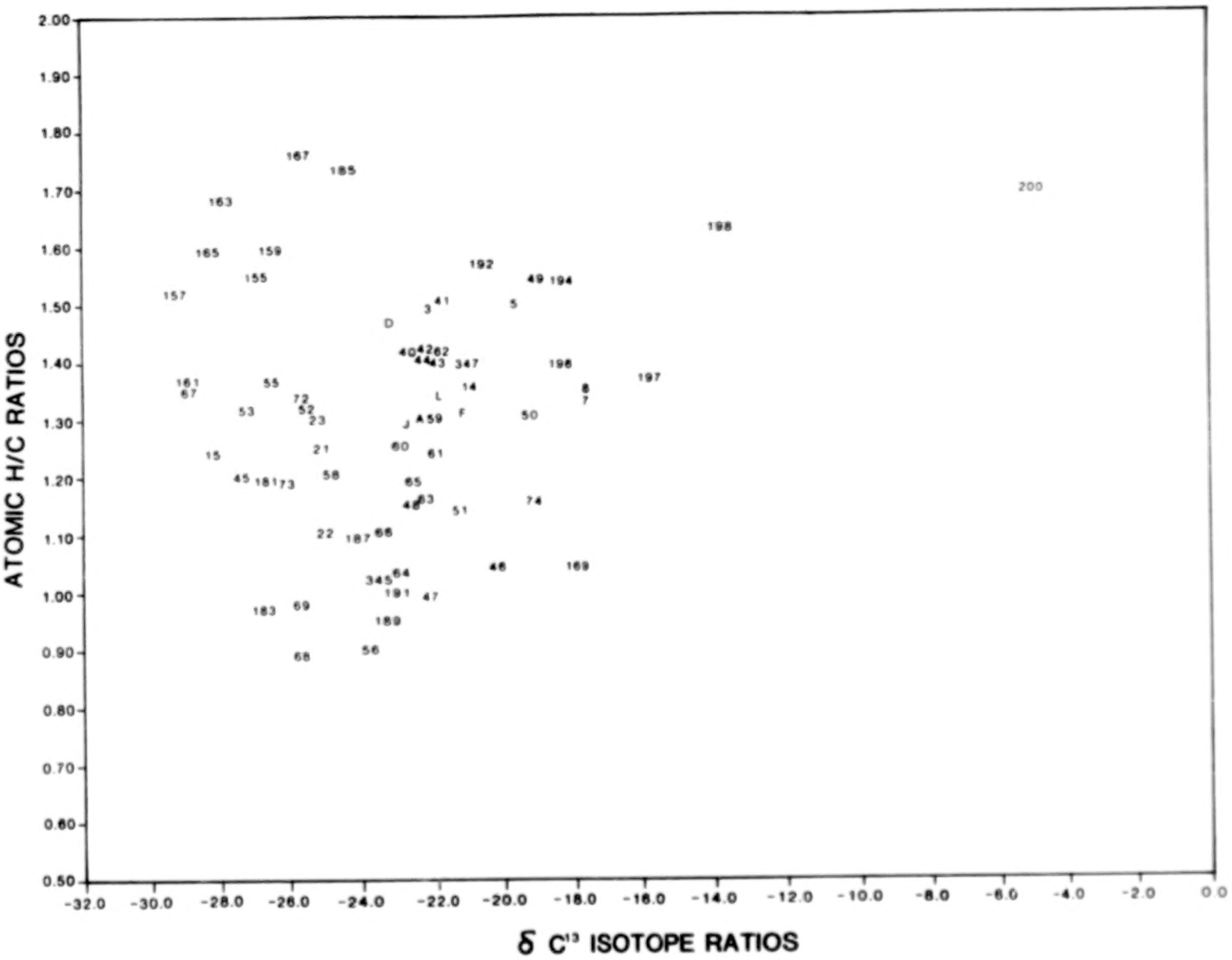

Figure 14.--Atomic H/C and δ^{13}C isotape ratios of humic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

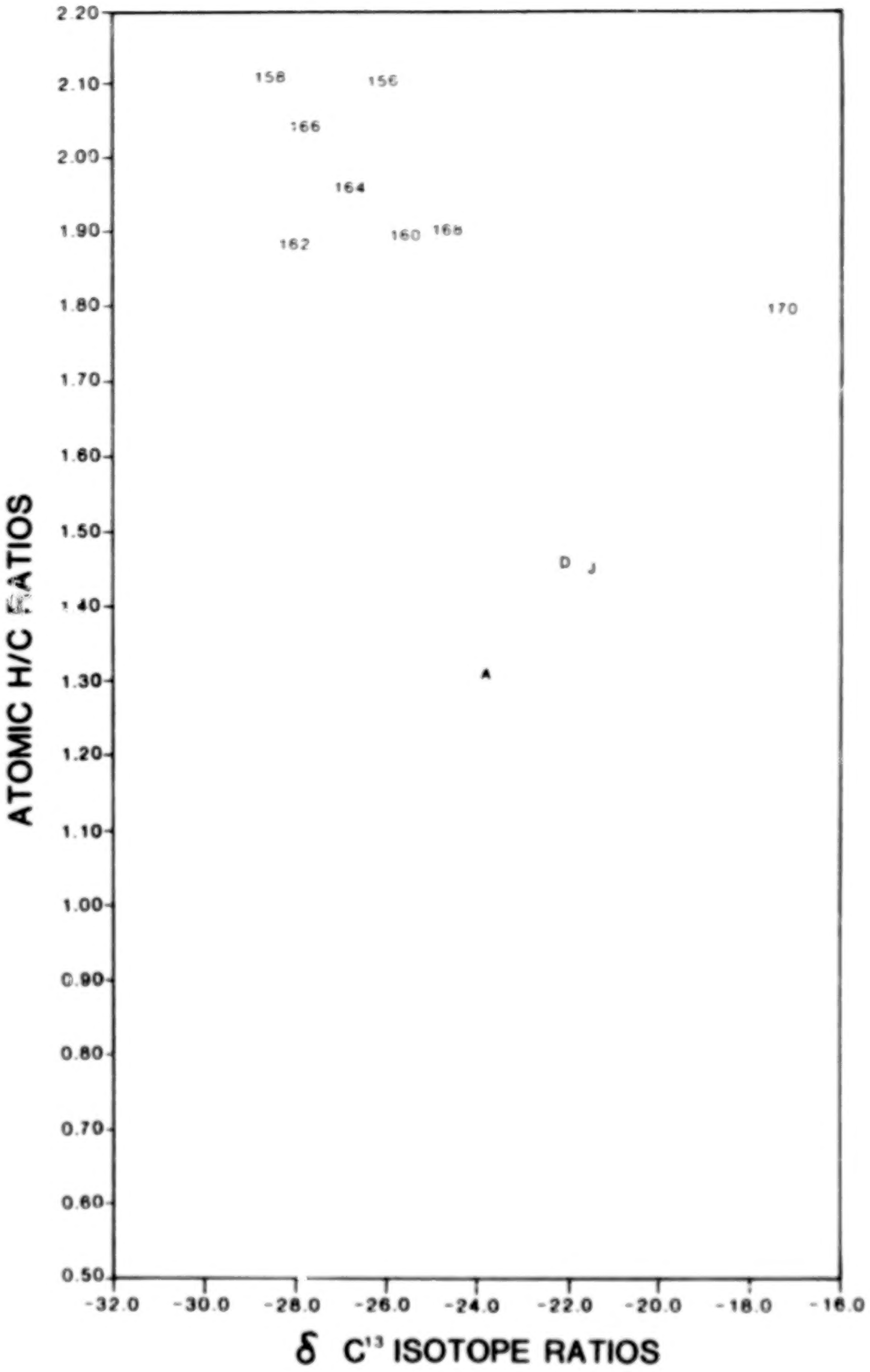

Figure 15.—Atomic H/C and $\delta^{13}C$ isotope ratios of fulvic acids from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

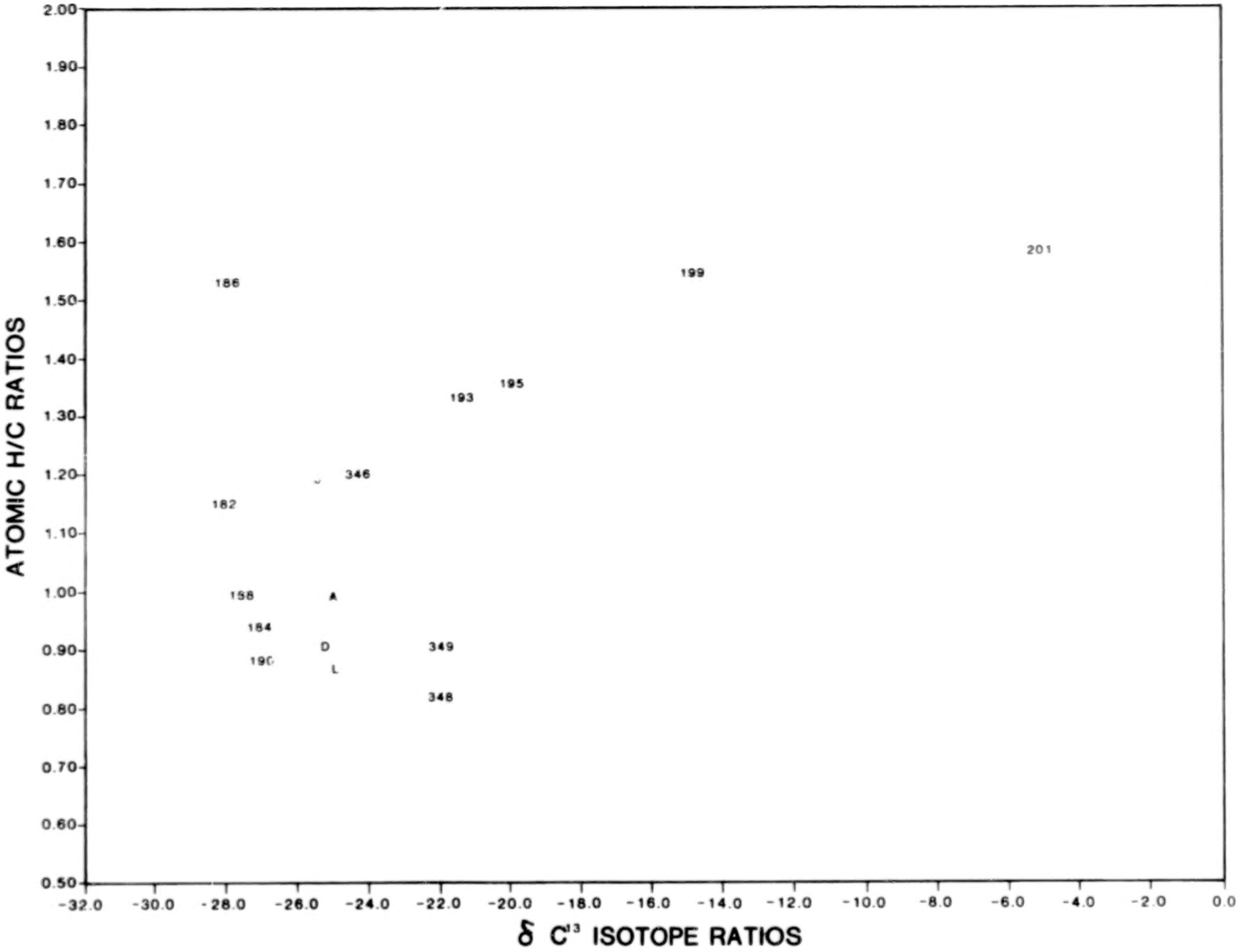

Figure 16.—Atomic H/C and $\delta^{13}C$ isotope ratios of protokerogens from soils and sediments. Numbers correspond to literature data in Appendix 1, letters represent this study.

average atomic H/C ratios of 1.33 and 1.36, respectively, the $\delta^{13}C$ isotopic ratios near -22 per mil, and the abundance of foraminifera observed in the sediment, suggest that the fulvic and humic acids may have been derived primarily from organic matter from a marine planktonic source. This result is consistent with the observations of Huc and Durand (1977) and Tissot and Welte (1978). The humic acids in this study were observed to be similar to humic acids reported in the literature on sediments from the Saanich Inlet (samples 59-65), Lake Haruna (sample 14), and several basins offshore California (samples 40-44) (fig. 14; appendix 1). There are, however, too few data reported on fulvic acids and protokerogens in the literature to make a comparison with the data in this study (figs. 15, 16).

Thermal Pyrolysis-Gas Chromatographic Analyses

Gas chromatograms of the pyrolysis products evolved at elevated temperatures from toluene-methanol extracted sediments, humic acids and protokerogens are presented in figure 17. The gas chromatograms of the pyrolysis products evolved from the extracted sediment from stations G-5 and K-4 show predominantly short carbon chain length products, although the products evolved from extracted sediment from stations G-6 and J-2 show an increased tendency for somewhat longer chain products. Bailey (1981) interpreted pyrolysis-gas chromatograms of amorphous, algal, herbaceous and woody kerogens and suggested that the longer carbon chain components were indicative of a more oil prone character of the organic matter. The predominantly short carbon chain length products evolved from the station G-5 and K-4 sediments are therefore interpreted to suggest the influence of predominantly woody, gas-prone organic component inputs to the sediments. A slightly increased influence of more lipoidal, gas-condensate-to-oil prone organic materials

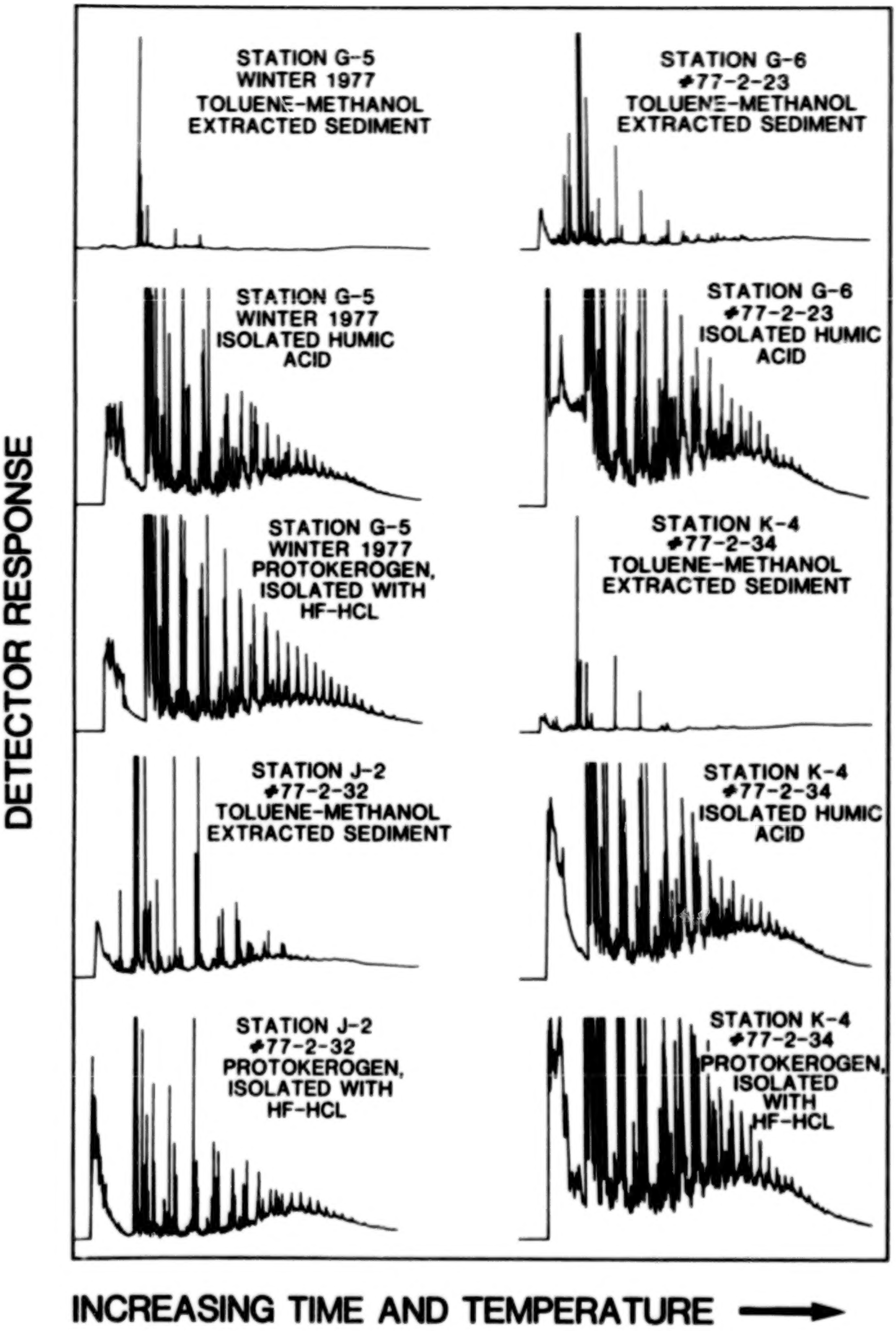

Figure 17.—Gas chromatograms of volatile thermal pyrolysis products evolved at elevated temperatures from extracted sediments and humic substances.

to the sediments at stations G-6 and J-2 is suggested based on the longer carbon chain pyrolysis products noted. Thermal pyrolysis products evolved from the humic acids isolated from stations G-5, G-6 and K-4 show a longer carbon chain length distribution and considerably more complex pattern than those products evolved from the extracted sediments from the same stations. In addition, the thermal pyrolysis products evolved from protokerogens isolated from station G-5, J-2 and K-4 sediments showed gas chromatographic patterns with a longer carbon chain length distribution and more complexity than the sediment pyrolysis patterns. The thermal pyrolysis products of the humic acids and protokerogens isolated from the same stations (G-5 and K-4) are nearly identical, which suggests a similarity in the character of the humic acid and protokerogen. It is believed that this data suggests that the humic substances include a gas-condensate-to-oil prone character.

Possible Formation Pathways

The possible interrelationship of the humic substances may be explained by two major pathways: (1) The fulvic and humic acids may be formed by the degradation of the protokerogens; this suggestion is analogous to the microbial synthesis concept discussed by Felbeck (1971) and Schnitzer and Khan (1972); (2) The humic substances may evolve through a succession of fulvic acid to humic acid to form a portion of the protokerogen (Tissot and Welte, 1978). Alternatively, fulvic acid, humic acid and protokerogen may not show a direct relationship.

The formation of the fulvic and humic acids in these samples is not believed to be the result of the oxidative degradation of the protokerogen. Isotope fractionation is believed to occur during oxidative degradation of organic matter due to kinetic effects and may result in products enriched in the ^{12}C

rather than the ^{13}C isotope (Galimov, 1980). The formation of the fulvic and humic acids, with an average $\delta^{13}C$ ratio of -22.4 per mil, from the degradation of the protokerogens, with an average $\delta^{13}C$ ratio of -25.2 per mil, would require either the addition of ^{13}C-enriched carbon or a preferential loss of ^{13}C-depleted carbon. These possibilities do not appear to be favored by the kinetic isotope effects discussed by Galimov (1980).

The elemental, infrared, and carbon isotopic evidence presented in this study suggests that a loss of O- and N-containing functional groups may occur during condensation and polymerization reactions in the formation of the humic substances. This interpretation is consistent with the suggestion of Tissot and Welte (1978) that the succession of fulvic to humic acid to protokerogen may be a significant evolutionary pathway of humic substances. The similarity of the pyrolysis-gas chromatograms of humic acids and protokerogens from stations G-5 and K-4 further support the interpretation of a direct relationship. The $\delta^{13}C$ isotopic ratio for the A-2 fulvic acid, however, was 1.4 per mil lighter than that of the humic acid, which is not consistent with the interpretation of the succession of fulvic acid to humic acid, and suggests that this succession may not be the only pathway.

It has been observed that humic and fulvic acids may be of lesser abundance in sediments with predominantly marine inputs as compared to sediments with inputs from higher plant sources (Huc and others, 1975; Tissot and Welte, 1978). Tissot and Welte (1978) have suggested that values of fulvic-plus-humic acids in sediments with terrestrial organic inputs may be as high as 70 percent whereas values in sediments with primarily marine-derived organic material are believed to be typically 10-15 percent. In this study, the concentrations of fulvic-plus-humic acids were low relative to the protokerogen-plus-hydrolyzable carbon (table 4, 5, and 6). Fulvic-plus-humic acids were less than

34 percent and averaged 16.7 percent of the total organic carbon and the average protokerogen-plus-hydrolyzable fraction was 83.3 percent of the total organic carbon. These data are consistent with the interpretation for a mainly marine organic input.

Several explanations can be offered to account for the relative proportions of the humic fractions observed in sediments: (1) Tissot and Welte (1978) have suggested that a part of the organic matter may be converted to protokerogen through a pathway which does not involve fulvic or humic acid stages. (2) A portion of the insoluble fraction may be of detrital origin which was reworked from previous deposits (Sackett and others, 1974; Tissot and Welte, 1978). (3) It is further proposed here that fulvic and humic acids may undergo rapid conversion to protokerogens in this depositional environment.

In this latter suggestion, the fulvic and humic acids are considered to be intermediates in the formation of protokerogens. Theoretically, the carbonium ions and radicals formed from aromatic compounds are stabilized by resonance in the aromatic structures (Morrison and Boyd, 1967, p. 392, 401). The increased resonance of these structures may tend to make the aromatic carbonium ion or radical intermediates more stable and less reactive than aliphatic intermediates. Humic substances derived primarily from marine sources are believed to have a greater aliphatic and lower aromatic structural character than humic substances derived from higher plant forms (Tissot and Welte, 1978; Dereppe and others, 1980; Larter and Douglas, 1980). The humic materials in this study are believed to be derived largely from marine organic sources. The hydrogen-rich nature of the humic and fulvic acids, as suggested by the average H/C ratio of 1.35, may be the result of precursor organic materials with a largely aliphatic structural framework. Without the stability from resonance suggested for aromatic intermediates, the largely aliphatic intermediates suggested for the formation pathway of the humic substances in this study may be more reactive and may undergo relatively rapid conversion to protokerogen. As a result of this increased reactivity, these depositional environments with primarily hydrogen-rich marine organic inputs may also show a lower abundance of fulvic-plus-humic acids than environments which may contain largely humic substances derived from higher plants. This interpretation is consistent with the relatively low fulvic-plus-humic acids observed in these samples.

Condensation-type pathways as discussed by Larter and Douglas (1980) and Harvey and others (1982) are suggested as possible models for the formation of a portion of the humic substances in this study. These models suggest that the organic source material may greatly influence the hydrogen-to-carbon ratio and the structural components of the humic substances, and that microbial activity may influence the rate of formation through availability of reactive components. The models further suggest that Eh-pH conditions of the depositional environment may affect the stability of the intermediate products, the rate of formation of the humic substances, and the relative abundance of the fulvic and humic acids and protokerogens.

Hoering (1973) observed that the melanoidin model predicted that humic substances should have a structural component based on furfural or furan, but that no definite evidence for the five-membered heterocyclic ring had been obtained. Harvey and others (1982) suggested that furan rings may also be formed during the conversion of polyunsaturated fatty acids to humic substances in the cross-linking model, although six-membered rings are thermodynamically favored. Several studies which involved the pyrolysis of humic substances have shown the presence of furans, methylfurans, and benzofurans among the products (Wershaw and Bohner, 1969; Bracewell and others, 1976; Sklarew, 1979; Van De Meent and others, 1980). The furan structures may, however, also be formed during pyrolysis by rearrangements at high temperatures. Liao and others (1982) observed furan carboxylic acids among the chemical degradation products of fulvic and humic acids isolated from lake water. The degradations were achieved via both $KMnO_4$ oxidation and NaOH hydrolysis of the humic material. Furan structures show a characteristic absorption in the 1020-1100 cm^{-1} spectral region (Bellamy, 1958). Absorption in this spectral region of the humic substances in this study may suggest the presence of furan-type structural components (figs. 11, 12, 13). Carbohydrate structures, however, may also show absorption in this same region. Therefore, clear evidence for furan structural components is lacking, and further study is needed to confirm the presence of such structures in humic substances in order to support an interpretation of a formation pathway via these models.

Protokerogens, possibly formed through the condensation and polymerization of fulvic and humic acids, may represent only a portion of the total protokerogen. The protokerogens in this study also consist of organic remnants which include wood fragments, plant tissues, pollen, spores, gelified tissues, and algal cell remains (E.Robbins, oral commun., 1981). The heterogenity of the protokerogens further suggests that the formation of the humic substances may follow complex pathways as proposed by Wilson and Goh (1981).

Durand and Monin (1980) described Type II kerogens as insoluble organic matter in sedimentary rocks which consists essentially of amorphous material, probably derived from planktonic biomass, with identifiable remains of organisms (less than 30 percent of the organic matter) including algal cells and ligneous debris in variable proportions. The description of the protokerogens isolated from the surface sediments in this study is consistent with that of Durand and Monin (1980) for Type II kerogens. The distinction between protokerogen and kerogen in this study is based on the relatively large hydrolyzable fraction of the organic matter and is consistent with the views expressed by Tissot and Welte (1978, p. 88). The protokerogens identified in this study are, therefore, believed to represent precursors for Type II kerogens. This interpretation is further supported by the pyrolysis-gas chromatographic patterns which suggest a gas-condensate-to-oil prone character of the humic acids and protokerogens analyzed. The H/C and O/C ratios of the protokerogens were generally in the range of Type II kerogens as given by Hunt (1979, p.274), although the H/C ratios from several samples were also within the range for Type III kerogens (fig. 18, adapted from Tissot and Welte, 1978). The apparent inconsistency may be due in part to a preferential acid hydrolysis of less resistant protokerogen as suggested by Durand and Nicaise (1980). The more resistant residue may contain a larger proportion of reworked, recycled, or higher plant materials which have lower H/C and lighter $\delta^{13}C$ ratios than the fraction which was hydrolyzed. On the basis of the van Krevelen type diagram of the elemental compositions and paths of evolution of the major types of kerogen the humic and fulvic acids in this study are also believed to generally fit the field of data for the Type II kerogen pathway and have generally higher H/C ratios than suggested for the Type III pathway.

CONCLUSIONS

Infrared spectroscopic, elemental and stable carbon isotopic characteristics of humic and fulvic acids and protokerogens isolated from Mid-Atlantic Continental Shelf and Slope surface sediments have been reported. Although much work remains to be done to determine the nature and formation pathways of the humic substances in surface sediments, several statements may be made to summarize this study.

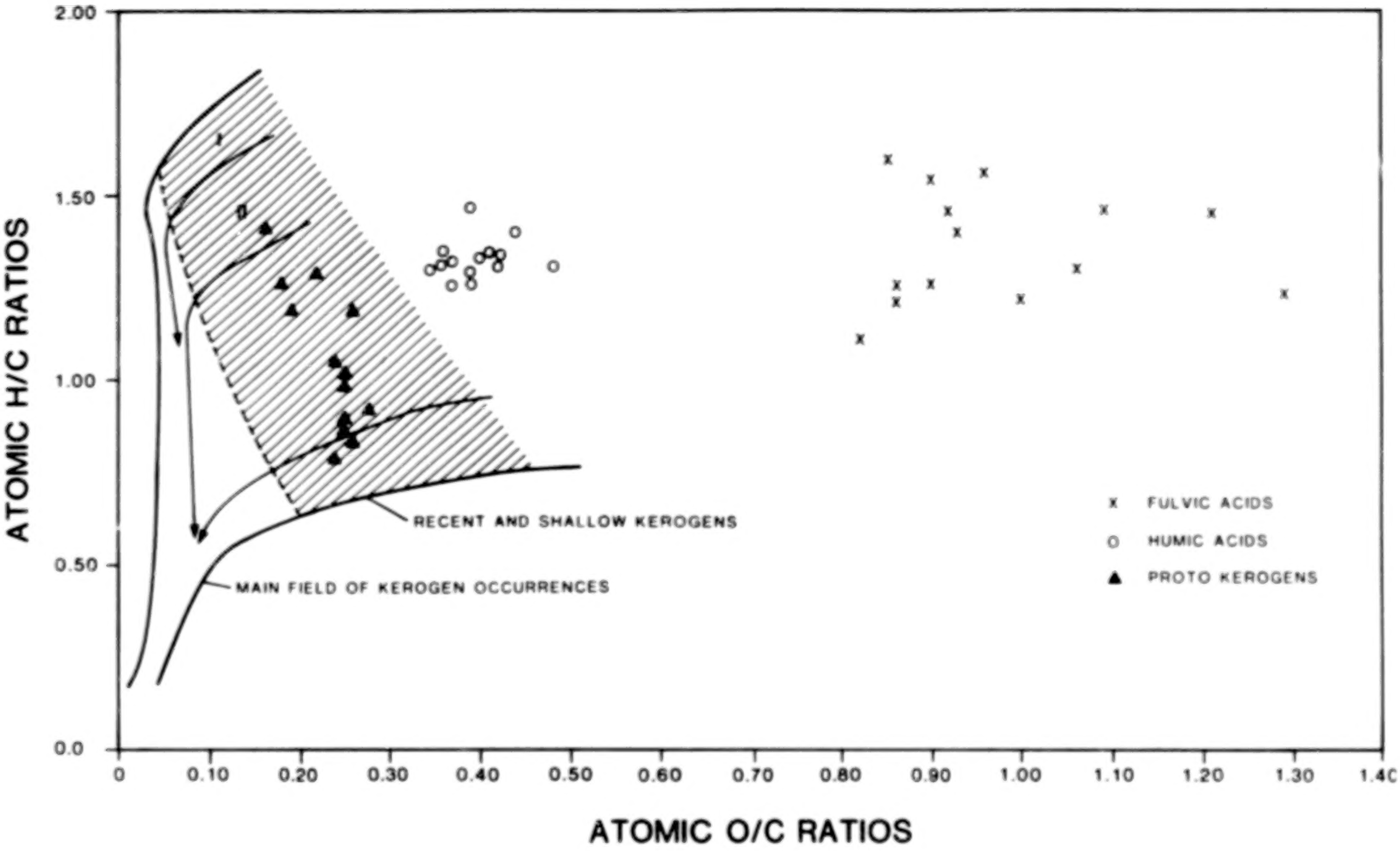

Figure 18.—Atomic H/C and O/C ratios of fulvic acids, humic acids, and protokerogens isolated in this study. The major types of kerogen and their paths of evolution are shown for comparison (adapted from Tissot and Welte, 1978, p. 87).

(1) The elemental compositions, atomic and isotopic ratios, and infrared spectra were similar for the humic acids at each station in this study. This similarity suggests that the humic acids isolated from the different shelf locations were derived from similar organic source materials.

(2) The humic and fulvic acids isolated from the sediments in this study were relatively hydrogen-rich, as suggested by the average H/C atomic ratios of 1.33 and 1.36, respectively, and by absorption bands in the infrared spectra attributed to aliphatic CH_2 and CH_3 groups (2920-2850 cm^{-1} wavelength region). The $\delta^{13}C$ isotopic ratios of the humic and fulvic acids averaged -22.4 per mil. It is suggested that the humic and fulvic acids are derived primarily from organic matter of marine origin. This interpretation is consistent with the observed elemental, pyrolysis-gas chromatographic, carbon isotopic, and infrared spectroscopic evidence, and is supported by the presence of abundant foraminiferal tests noted in the sediment.

(3) The $\delta^{13}C$ isotopic ratios of the protokerogens averaged -25.2 per mil and were isotopically lighter than the humic and fulvic acids. This difference between the humic and fulvic acids and protokerogens may indicate: (1) isotopic fractionation of the organic matter during formation of the protokerogens or through acid hydrolysis of the less resistant organic matter during isolation of the protokerogens or (2) a progression of humic and fulvic acids to protokerogens through a loss of ^{13}C-enriched functional groups. The protokerogens may be in part derived from reworked organic matter.

(4) Interpretation of the analytical results suggests a largely marine organic source for the humic substances in these sediments, although the presence of identifiable organic materials in the protokerogens included woody tissues, pollen and spores. The humic substances were relatively hydrogen-rich , gas condensate-to-oil prone and may represent precursors for the formation of

Type II kerogens.

(5) The succession of fulvic acids to humic acids to protokerogens is believed to be a significant evolutionary pathway for a portion of the protokerogens examined in this study.

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REFERENCES

Bailey, N.J.L., 1981, Hydrocarbon potential of organic matter, in J. Brooks, ed., Organic maturation studies and fossil fuel exploration: New York, Academic Press, p. 283-302.

Bellamy, L.J., 1958, The infrared spectra of complex molecules: London, Methuen and Co., 425 p.

Bordovskiy, O.K., 1965, Accumulation and transformation of organic substances in marine sediments: Marine Geology, v. 3, p. 3-114.

Bracewell, J.M., Robertson, G.W., and Tate, K.R., 1976, Pyrolysis-gas chromatography studies on a climosequence of soils in tussock grasslands, New Zealand: Geoderma, v. 15, p. 209-215.

Burreson, E.M., 1979, Chemical and biological benchmark studies, executive summary report, in Middle Atlantic Outer Continental Shelf environmental studies. Volume I, Executive Summary: Gloucester Point, Virginia Institute of Marine Science, p. 1-129.

Craig, H.D., 1953, The geochemistry of stable carbon isotopes: Geochimica et Cosmochimica Acta, v. 3, p. 53-92.

Debyser, Y., Pelet, R., and Dastillung, M., 1977a, Geochimie organique de sediments marins recents, in Campos, R., and Goni, J., eds., Advances in organic geochemistry 1975: Madrid, Spain, Empresa Nacional Adaro de Investigaciones Mineras, p. 289-320.

Debyser, Y., Gadel, F., Rebeller, R., LeBlond, C., Okhimian, D., Cambon, F., Cauwet, G., and Cambon, J. P., 1977b, Etude geochimique des composes humiques et des kerogenes, in Geochimie organique des sediments marins profonds: Paris, Editions du Centre National de la Recherche Scientifique, p. 247-268.

Degens, E.T., 1969, Biogeochemistry of stable carbon isotopes, in Eglinton, G., and Murphy, M.T.J., eds., Organic geochemistry: methods and results: New York, Springer-Verlag, p. 304-329.

Degens, E.T., Guillard, R.R.L., Sackett, W.M., and Hellebust, J.A., 1968, Metabolic fractionation of carbon isotopes in marine plankton - I. Temperature and respiration experiments: Deep-Sea Research, v. 15, p. 1-9.

Dereppe, J.M., Moreaux, C., and Debyser, Y., 1980, Investigation of marine and terrestrial humic substances by ^{1}H and ^{13}C nulcear magnetic resonance spectroscopy: Organic Geochemistry, v. 2, p. 117-124.

Durand, B., and Espitalie, J., 1976, Geochemical studies on the organic matter from the Douala Basin (Cameroun) - II. Evolution of kerogen: Geochimica et Cosmochimica Acta, v. 40, p. 801-808.

Durand, B., and Monin, J.C., 1980, Elemental analysis of kerogens (C,H,O,N,S,Fe), in Durand, B., ed., Kerogen, insoluble organic matter from sedimentary rocks: Paris, France, Editions Technip, p. 113-138.

Durand, B., and Nicaise, G., 1980, Procedures for kerogen isolation, in Durand, B., ed., Kerogen, insoluble organic matter from sedimentary rocks: Paris, France, Editions Technip, p. 35-53.

Felbeck, G.T., 1971, in McLaren, A.D., and Skujins, J., eds, Soil biochemistry, v. 2: New York, Marcel Decker, p. 55-56.

Forsman, J.P., and Hunt, J.M., 1958, Insoluble organic matter (kerogen) in sedimentary rocks: Geochimica et Cosmochimica Acta, v. 15, p. 170-182.

Galimov, E.M., 1974, Organic geochemistry of carbon isotopes, in Tissot, B., and Bienner, F., eds., Advances in organic geochemistry 1973: Paris, France, Editions Technip, p. 439-452.

Galimov, E.M., 1980, C^{13}/C^{12} in kerogen, in Durand, B., ed., Kerogen, insoluble organic matter in sedimentary rocks: Paris, France, Editions Technip, p. 271-299.

Goh, K.M., and Stevenson, F.J., 1971, Comparison of infrared spectra of synthetic and natural humic and fulvic acids: Soil Science, v. 112, p. 392-400.

Grant, D., 1977, Chemical structure of humic substances: Nature, v. 270, p. 707-710.

Griffith, S.M., and Schnitzer, M., 1975, Analytical characteristics of humic and fulvic acids extracted from tropical volcanic soils: Soil Science Society of America Proceedings, v. 39, p. 861-867.

Harvey, G.R., Boran, D.A., Chesal, L.A., and Tokar, J.M., 1982, The structure of marine fulvic and humic acids: Marine Chemistry, v. 12, p. 119-132.

Hatcher, P.G., Rowan, R., and Mattingly, M.A., 1980a, ^{1}H and ^{13}C NMR of marine humic acids: Organic Geochemistry, v. 2, p. 77-85.

Hatcher, P.G., VanderHart, D.L., and Earl, W.L., 1980b, Use of solid-state ^{13}C NMR in structural studies of humic acids and humin from Holocene sediments: Organic Geochemistry, v. 2, p. 87-92.

Hatcher, P.G., Breger, I.A., and Mattingly, M.A., 1980c, Structural characteristics of fulvic acids from Continental Shelf sediments: Nature, v. 285, p. 560-562.

Hatcher, P.G., Maciel, G.E., and Dennis, L.W., 1981, Aliphatic structure of humic acids; a clue to their origin: Organic Geochemistry, v. 3, p. 43-48.

Hoering, T.C., 1973, A comparison of melanoidin and humic acid: Carnegie Institution of Washington, Yearbook 72, 1972-73, p. 682-690.

Holtzclaw, K.M., Sposito, G., and Bradford, G.R., 1976, Analytical properties of the soluble, metal-complexing fractions in sludge-soil mixtures: extraction and purification of fulvic acid: Soil Science Society of America Proceedings, v. 40, p. 254-258.

Huc, A.Y., and Durand, B., 1977, Occurrence and significance of humic acids in ancient sediments: Fuel, v. 56, p. 73-80.

Huc, A.Y., Durand, B., and Monin, J.C., 1975, Humic compounds and kerogens in cores from Black Sea sediments, Leg 42B - Holes 379A, B, and 380A, in Usher, J.L., and Supko, P., eds., Initial reports of the Deep Sea Drilling Project, v. 42, part 2: Washington, U.S. Government Printing Office, p. 737-748.

Hunt, J.M., 1979, Petroleum geochemistry and geology: San Francisco, W.H. Freeman, 617 p.

Ishiwitari, R., 1973, Chemical characterization of fractionated humic acids from lake and marine sediments: Chemical Geology, v. 12, p. 113-126.

Khan, S.U., and Schnitizer, M., 1972, Permanganate oxidation of humic acids, fulvic acids and humins extracted from Ah horizons of a Black Chernozem, a Black Solod and a Black Solonetz soil: Canadian Journal of Soil Science, v. 52, p. 43-51.

Khan, S.U., and Sowden, F.J., 1971, Distribution of nitrogen in the Black Solonetzic and Black Chernozemic soil of Alberta: Canadian Journal of Soil Science, v. 51, p. 185-193.

Knebel, H.J., 1979, Geologic studies, executive summary report, in Middle Atlantic Outer Continental Shelf environmental studies, volume 1, executive summary: Gloucester Point, Virginia Institute of Marine Science, p. 130-152.

Knebel, H.J., and Folger, D.W., 1976, Large sand waves on the Atlantic Outer Continental Shelf around Wilmington Canyon, off eastern United States: Marine Geology, v. 22, p. M7-M15.

Knebel, H.J., and Spiker, E., 1977, Thickness and age of surficial sand sheet, Baltimore Canyon Trough area: American Association of Petroleum Geologists Bulletin, v. 61, p. 861-871.

Kononova, M., 1966, Soil organic matter: Oxford, Pergamon, 523 p.

Kononova, M.M., and Bel'chikova, N.P., 1961, Quick methods for determining the humus composition of mineral soils: Soviet Soil Science (English translation), p. 1112-1121.

Larter, S.R., and Douglas, Q.G., 1980, Melanoidins - kerogen precursors and geochemical lipid sinks: a study using pyrolysis gas chromatography (PGC): Geochimica et Cosmochimica Acta, v. 44, p. 2087-2095.

Liao, W., Christman, R.F., Johnson, J.D., and Millington, D.S., 1982, Structural characterization of aquatic humic material: Environmental Science and Technology, v. 16, p. 403-410.

Long, G., Neglia, S., and Favretto, L., 1968, The metamorphism of the kerogen from Triassic Black Shales, southeast Sicily: Geochimica et Cosmochimica Acta, v. 32, p. 647-656.

Maillard, L.C., 1912, Action des acides amines sur les sucres; formation des melanoidines par votre methodiques: C.R. Acadamie of Science, v. 154, p. 66-68.

Malcolm, R.L., 1976, Method and importance of obtaining humic and fulvic acids of high purity: U.S. Geological Survey Journal of Research, v. 4, p. 37-40.

Manskaya, S.M., and Drozdova, T.V., 1968, Geochemistry of organic substances, Shapiro, L., and Breger, I.A., trans. and eds.: London, Pergamon, 345 p.

Miller, R.E., Schultz, D.M., Lerch, H., Ligon, D., Owings, D., and Gary, C., 1979a, Hydrocarbon geochemical analyses of mid-Atlantic Outer Continental Shelf sediments: an environmental assessment: U.S. Geological Survey open-file report 79-363, p. 1-41.

Miller, R.E., Schultz, D.M., Claypool, G.E., Smith, M.A., Lerch, H.E., Ligon, D., Gary, C., and Owings, D.K., 1979b, Organic geochemistry, in Scholle, P.A., ed., Geological studies of the COST GE-1 Well, United States South Atlantic Outer Continental Shelf area: U.S. Geological Survey Circular 800, p. 74-92.

Morrison, R.T., and Boyd, R.N., 1967, Organic chemistry, second edition: Boston, Mass., Allyn and Bacon, 1204 p.

Nissenbaum, A., 1974, The organic geochemistry of marine and terrestrial humic substances: implications of carbon and hydrogen isotope studies, in Tissot, B., and Bienner, F., eds., Advances in organic geochemistry 1973: Paris, France, Editions Technip, p. 39-51.

Nissenbaum, A., and Kaplan, I.R., 1972, Chemical and isotopic evidence for the in situ origin of humic substances: Limnology and Oceanography, v. 17, p. 570-582.

Nissenbaum, A., and Swaine, D.J., 1976, Organic matter-metal interactions in Recent sediments: the role of humic substances: Geochimica et Cosmoshimica Acta, v. 40, p. 809-816.

Otsuki, A., and Hanya, T., 1967, Some precursors of humic acid in Recent lake sediment suggested by infra-red spectra: Geochimica et Cosmochimica Acta, v. 31, p. 1505-1515.

Philp, R.P., and Calvin, M., 1976, Possible origin for insoluble organic (kerogen) debris in sediments from insoluble cell-wall materials of algae and bacteria: Nature, v. 262, p. 134-136.

Reineck, H.E., and Singh, I.B., 1980, Depositional sedimentary environments: New York, Springer-Verlag, 549 p.

Riffaldi, R., and Schnitzer, M., 1972, Electron spin resonance spectrometry of humic substances: Soil Science Society of America Proceedings, v. 36, p. 301-305.

Rouxhet, P.G., Robin, P.L., and Nicaise, G., 1980, Characterization of kerogens and of their evolution by infrared spectroscopy, in Durand, B., ed., Kerogen, insoluble organic matter from sedimentary rocks: Paris, France, Editions Technip, p. 163-190.

Ruzecki, E.P., Welch, C.S., and Baker, D.L., 1977, Physical oceanography and climatology, in Middle Atlantic Outer Continental Shelf environmental studies. Volume II - A. Chemical and biological benchmark studies: Gloucester Point, Virginia Institute of Marine Science, p. 3-1 to 3-71.

Sackett, W.M., Eckelmann, W.R., Bender, M.L., and Be, A.W.H., 1965, Temperature dependence of carbon isotope compositions in marine plankton and sediments: Science, v. 148, p. 235-237.

Sackett, W.M., Poag, C.W., and Eadie, B.J., 1974, Kerogen recycling in the Ross Sea, Antarctica: Science, v. 185, p. 1045-1047.

Sackett, W.M., and Thompson, R.R., 1963, Isotopic organic carbon composition of recent continental derived clastic sediments of the eastern Gulf Coast, Gulf of Mexico: American Association of Petroleum Geologists Bulletin, v. 47, p. 525-531.

Saxby, J. D., 1970, Isolation of kerogen in sediments by chemical methods: Chemical Geology, v. 6, p. 173-184.

Schlee, J.S., 1981, Seismic stratigraphy of Baltimore Canyon Trough: American Association of Petroleum Geologists Bulletin, v. 65, p. 26-53.

Schnitzer, M., 1969, Reactions between fulvic acid, a soil humic compound and inorganic soil constituents: Soil Science Society of America Proceedings, v. 33, p. 75-81.

Schnitzer, M., and Hoffman, I., 1967, Thermogravimetric analysis of the salts and metal complexes of a soil fulvic acid: Geochimica et Cosmochimica Acta, v. 31, p. 7-15.

Schnitzer, M., and Khan, S.U., 1972, Humic substances in the environment: New York, Marcel Dekker, 311 p.

_____, eds., 1978, Soil organic matter: New York, Elsevier, 319 p.

Schnitzer, M., and Kodama, H., 1972, Reactions between fulvic acid and Cu^{2+}--montmorillonite: Clays and Clay Mineralogy, v. 20, p. 359-367.

Scholle, P.A., ed., 1977, Geological studies on the COST No. B-2 Well, U.S. Mid-Atlantic Outer Continental Shelf area: U.S. Geological Survey Circular 750, p. 1-71.

Scholle, P.A., ed., 1980, Geological studies on the COST No. B-3 Well, United States Mid-Atlantic Continental Slope area: U.S. Geological Survey Circular 833, p. 1-112.

Segar, D.A., and Berberian, G.A., 1976, Oxygen depletion in the New York Bight apex: Causes and consequences, in Gross, M.G., ed., Middle Atlantic Continental Shelf and the New York Bight, American Society of Limnology and Oceanography Special Symposia, v. 2: Lawrence, Kansas, Allen Press, p. 220-239.

Slarew, D.S., 1979, Analysis and simulated diagenesis of kerogen in a Recent bottom mud from Mono Lake, California: a comparison with selected ancient kerogens; Geochimica et Cosmochimica Acta, v. 43, p. 1949-1958.

Smith, J.W., 1961, Ultimate composition of organic material in Green River oil shale: U.S. Department of the Interior, Bureau of Mines, Report of Investigations 5725, p. 1-16.

Stevenson, F.J., and Butler, J.H.A., 1970, Chemistry of humic acids and related pigments, in Eglinton, G., and Murphy, M.T.J., eds., Organic geochemistry: methods and results: New York, Springer-Verlag, p. 534-557.

Stevenson, F.J., and Goh, K.M., 1971, Infrared spectra of humic acids and related substances: Geochimica et Cosmochimica Acta, v. 35, p. 471-483.

Stuermer, D.H., Peters, K.E., and Kaplan, I.R., 1978, Source indicators of humic substances and proto-kerogen. Stable isotope ratios, elemental compositions and electron spin resonance spectra: Geochimica et Cosmochimica Acta, v. 42, p. 989-997.

Swift, D.J.P., 1969, Outer shelf sedimentation: processes and products, in The new concepts of continental margin sedimentation: Application to the geological record, American Geological Institute short course: Washington, American Geological Institute, Lecture 5, p. 5-1 to 5-26.

Swift, D.J.P., Freeland, G.L., Gadd, P.E., Han, G., Lavelle, J.W., and Stubblefield, W.L., 1976, Morphologic evolution and coastal sand transport, New York - New Jersey Shelf, in Gross, M.G., ed., Middle Atlantic Continental Shelf and the New York Bight, American Society of Limnology and Oceanography Special Symposia, v. 2: Lawrence, Kansas, Allen Press, p. 69-89.

Tissot, B.P., and Welte, D.H., 1978, Petroleum formation and occurrence: New York, Springer-Verlag, 538 p.

Van De Meent, D., Brown, S.C., Philps, R.P., and Simoneit, B.R.T., 1980, Pyrolysis-high resolution gas chromatography and pyrolysis gas chromatography-mass spectrometry of kerogens and kerogen precursors: Geochimica et Cosmochimica Acta, v. 44, p. 999-1013.

Wershaw, R.L., and Bohner, G.E., Jr., 1969, Pyrolysis of humic and fulvic acids: Geochimica et Cosmochimica Acta, v. 33, p. 757-762.

Wilson, M.A., and Goh, K.M., 1981, Comment on the paper: "[^{1}H] and [^{13}C] NMR studies on the importance of aromatic structures in fulvic and humic acids" (Ruggiero and others, 1979): Geochimica et Cosmochimica Acta, v. 45, p. 489-492.

Wilson, M.A., Jones, A.J., and Williamson, B., 1978, Nuclear magnetic resonance spectroscopy of humic materials: Nature, v. 276, p. 487-489.

Appendix 1 - Data reported in the literature on elemental atomic and isotopic ratios of humic acids, fulvic acids and protokerogens.

Appendix 1 - Data reported in the literature on elemental atomic and isotopic ratios of fulvic acids, humic acids, and protokerogens.

Sample Number	Humic Substance* and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
1	HA, KC 1244A, Cow Pen, Scotian Shelf, 198 m water depth.	Rashid and King, 1969, 1971	1.26	0.48	0.088	--**	--	--	--
2	FA as above KC 1244A.	Rashid and King, 1969, 1971.	1.49	0.64	0.060	--	--	--	--
3	HA, KC 84, Emerald Basin, Scotian Shelf, 294 m water.	Rashid and King, 1969, 1971: Nissenbaum and Kaplan, 1972.	1.49	0.50	0.091	--	-22.2	--	--
4	FA as above, KC 84	Rashid and King, 1970.	1.70	0.69	0.084	--	--	--	--
5	HA, KC 66, Emerald Basin, Scotian Shelf, 241 m water.	Rashid and King, 1970; Nissenbaum and Kaplan, 1972.	1.50	0.44	0.075	--	-19.7	--	--
6	FA as above, KC 66	Rashid and King, 1970.	1.60	0.75	0.100	--	--	--	--
7	HA, 68-2-2-1, Cariaco, beyond sill of trench, 808 m water.	Rashid and King, 1970; Nissenbaum and Kaplan, 1972.	1.33	0.61	0.062	--	-17.2	--	--
8	HA 68-2-1-1, Cariaco trench, 1390 m water.	Rashid and King, 1970; Nissenbaum and Kaplan, 1972.	1.35	0.46	0.076	--	-17.2	--	--

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*HA = Humic acid; FA = Fulvic acid; Pk = Protokerogen, also termed humin and kerogen in the literature.

**Not reported

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios H/C	O/C	N/C	S/C	Isotope Ratios ^{13}C	^{15}N	D
9	FA as above, 68-2-1-1.	Rashid and King, 1970.	1.33	1.07	0.063	--	--	--	--
10	HA, Musquodoboit Harbor, Nova Scotia, 2 m water.	Rashid and King, 1970.	1.44	0.50	0.061	--	--	--	--
11	FA as above, Musquodoboit Harbor.	Rashid and King, 1970.	1.65	0.70	0.047	--	--	--	--
12	HA, Musquodoboit Harbor, Podzol soil under forest	Rashid and King, 1970.	1.28	0.55	0.061	--	--	--	--
13	FA as above, Musquodoboit Podzol.	Rashid and King, 1970.	0.78	0.70	0.030	--	--	--	--
14	HA, Lake Haruna, Japan	Otsuki and Hanya, 1967; Nissenbaum and Kaplan, 1972.	1.36	0.48	0.091	--	-21.0	--	--
15	HA, soil near Lake Haruna, station 2, under oak forest.	Otsuki and Hanya, 1967; Nissenbaum and Kaplan, 1972.	1.24	0.45	0.058	--	-28.2	--	--
16	HA, soil near Lake Haruna, station 3.	Otsuki and Hanya, 1967.	1.21	0.44	0.052	--	--	--	--
17	HA, Lake Haruna, Japan.	Ishiwitari, 1973.	1.37	0.48	0.116	--	--	--	--
18	HA, Lake Kizaki, Japan.	Ishiwitari, 1973.	1.00	0.49	0.062	--	--	--	--
19	HA, M-1, offshore Kii Pennisula, 500 m water depth.	Ishiwitari, 1973.	1.19	0.55	0.077	--	--	--	--
20	HA, M-2, Sagami Bay, Japan, 1100 m water.	Ishiwitari, 1973.	1.23	0.58	0.082	--	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
21	HA, Ein Gedi, Israel, Dead Sea, 330 m water.	Nissenbaum and others, 1972.	1.25	0.34	0.036	0.034	-25.1	--	--
22	HA, Masada, Dead Sea, 165 m water.	Nissenbaum and others, 1972.	1.11	0.46	0.025	0.014	-25.0	--	--
23	HA, Dead Sea, soil around shore.	Nissenbaum and others, 1972; Nissenbaum, 1974.	1.30	0.53	0.048	0.014	-25.2	--	-74.6
24	HA, Lake Ontario, near eastern end, 26 m water.	Kemp and Mudrochova, 1973.	--	--	0.099	--	--	--	--
25	FA as above, Lake Ontario.	Kemp and Mudrochova, 1973.	--	--	0.151	--	--	--	--
26	HA, Black Sea, station 1462K, 0.40 m depth in sediment.	Debyser and others, 1977a.	1.50	0.59	0.082	0.021	--	--	--
27	HA, Black Sea, station 1462K, 0.55 m depth in sediment.	Debyser and others, 1977a.	1.45	0.52	0.086	0.019	--	--	--
28	HA, Black Sea, station 1462K, 0.62 m depth in sediment.	Debyser and others, 1977a.	1.43	0.47	0.084	0.019	--	--	--
29	HA, Black Sea, station 1474K, 0.40 m depth in sediment.	Debyser and others, 1977a.	1.49	0.63	0.072	0.031	--	--	--
30	HA, Black Sea, station 1474K, 2.35 m depth in sediment.	Debyser and others, 1977a.	1.34	0.47	0.058	0.017	--	--	--
31	HA, Black Sea, station 1474K, 2.75 m depth in sediment.	Debyser and others, 1977a.	1.36	0.49	0.049	0.018	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
32	HA, Mauritania, off coast, station 12392-1, 0.09 m depth in sediment	Debyser and others, 1977a.	1.45	0.75	0.083	0.020	--	--	--
33	HA, Mauritania, station 12392-1, 0.5 m depth in sediment.	Debyser and others, 1977a.	1.54	0.55	0.075	0.028	--	--	--
34	HA, Mauritania, station 12392-1, 1.5 m depth in sediment.	Debyser and others, 1977a.	1.33	0.44	0.081	0.033	--	--	--
35	HA, Mauritania, station 12392-1, 3.63 m depth in sediment.	Debyser and others, 1977a.	1.34	0.51	0.081	0.025	--	--	--
36	HA, Mauritania, station 12392-1, 7.70 m depth in sediment.	Debyser and others, 1977a.	1.47	0.49	0.073	0.017	--	--	--
37	HA, Baltic Sea, station 101854, 0.35 m depth in sediment.	Debyser and others, 1977a.	1.41	0.57	0.077	0.030	--	--	--
38	HA, station 101854 2.0 m depth in sediment.	Debyser and others, 1977a.	1.18	0.47	0.076	0.017	--	--	--
39	HA, station 101854 3.2 m depth in sediment.	Debyser and others, 1977a.	1.27	0.47	0.068	0.020	--	--	--
40	HA, San Pedro Basin, off southern Calif. >200 m water.	Nissenbaum and Kaplan, 1972.	1.42	0.49	0.062	0.009	-22.7	--	-104.3
41	HA, Santa Cruz Basin, off southern Calif., >200 m water.	Nissenbaum and Kaplan, 1972.	1.51	0.51	0.086	0.007	-21.8	--	-110

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
42	HA, Santa Barbara Basin, off southern Calif., >200 m water.	Nissenbaum and Kaplan, 1972.	1.42	0.45	0.072	0.015	-22.5	--	-101.8
43	HA, Tanner Basin, off southern Calif., >200 m water depth.	Nissenbaum and Kaplan, 1972.	1.40	0.51	0.077	0.009	-22.0	--	-102.1
44	HA, Long Basin, off southern Calif., >200 m water depth.	Nissenbaum and Kaplan, 1972.	1.41	0.53	0.077	0.006	-22.3	--	--
45	HA, Santa Monica Basin, off southern Calif., >200 m water.	Nissenbaum and Kaplan, 1972.	1.20	0.35	0.091	0.011	-27.4	--	--
46	HA, Gulf of Calif., Mazatlan Basin.	Nissenbaum and Kaplan, 1972.	1.04	--	--	--	-20.2	--	--
47	HA, Pacific Ocean, off Oregon, 120 km offshore.	Nissenbaum and Kaplan, 1972.	0.99	--	--	--	-22.1	--	--
48	HA, Pacific Ocean, off Oregon, 160 km offshore.	Nissenbaum and Kaplan, 1972.	1.15	--	--	--	-22.5	--	-106.8
49	HA, Newport March, southern Calif.	Nissenbaum and Kaplan, 1972.	1.54	0.48	0.118	0.017	-19.1	--	-78.3
50	HA, tidal marsh NE Gulf of Mexico, sample 1.	Nissenbaum and Kaplan, 1972.	1.31	--	--	--	-19.3	--	--
51	HA, tidal marsh, NE Gulf of Mexico, sample 2.	Nissenbaum and Kaplan, 1972; Palacas and others, 1968.	1.14	--	--	--	-21.2	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
52	HA, Gulf of Paria, New Dragon's Mouth, Venezuela.	Nissenbaum and Kaplan, 1972.	1.32	0.42	0.082	0.050	-25.5	--	--
53	HA, estuary of the Amazon River.	Nissenbaum and Kaplan, 1972.	1.32	--	--	--	-27.3	--	--
54	HA, Choctawatchee Bay, Gulf of Mexico, sample 1.	Nissenbaum and Kaplan, 1972.	--	--	0.008	0.002	-25.3	--	--
55	HA, Amazon River sediment.	Nissenbaum and Kaplan, 1972.	1.37	0.52	0.081	0.001	-26.5	--	--
56	HA, North Dakota lignite.	Nissenbaum and Kaplan, 1972.	0.90	0.45	0.015	0.016	-23.8	--	--
57	melanoidin.	Nissenbaum and Kaplan, 1972.	1.53	0.40	0.069	--	--	--	--
58	HA, Minnesota peat.	Nissenbaum and Kaplan, 1972; Nissenbaum, 1974.	1.21	0.48	0.026	0.003	-24.9	--	-75.1
59	HA, Saanich Inlet, core no. 1, 0-15 cm depth in sediment.	Brown and others, 1972.	1.30	0.39	0.039	--	-22.1	--	--
60	HA, Saanich Inlet, core no. 1, 175-185 cm depth in sediment.	Brown and others, 1972.	1.26	0.45	0.059	0.058	-23.0	--	--
61	HA, Saanich Inlet, core no. 4, 0-15 cm depth in sediment.	Brown and others, 1972; Nissenbaum and Kaplan, 1972.	1.24	0.39	0.033	0.039	-22.0	--	-103.8

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
62	HA, Saanich Inlet, core no. 4, 240-250 cm depth in sediment.	Brown and others, 1972.	1.42	0.38	0.052	0.031	-21.9	--	--
63	HA, Saanich Inlet, core no. 3B, 790-820 cm depth in sediment.	Brown and others, 1972.	1.16	0.39	0.038	0.038	-22.4	--	--
64	HA, Saanich Inlet, core no. 3B, 1710-1740 cm depth in sediment.	Brown and others, 1972.	1.03	0.47	0.025	0.034	-23.1	--	--
65	HA, Saanich Inlet, core no. 3B, 2620-2650 cm depth in sediment.	Brown and others, 1972.	1.19	0.39	0.023	0.026	-22.7	--	--
66	HA, Saanich Inlet, core no. 3B, 3450-3480 cm depth in sediment.	Brown and others, 1972.	1.11	0.42	0.022	0.019	-23.4	--	--
67	HA, Saanich Inlet, forest soil.	Brown and others, 1972; Nissenbaum and Kaplan, 1972; Nissenbaum, 1974.	1.35	0.47	0.055	0.003	-29.1	--	-97.0
68	HA, humate cemented sands, northwest Florida, station 562-38A.	Swanson and Palacas, 1965; Nissenbaum and Kaplan, 1972.	0.89	0.51	0.030	0.004	-25.7	--	--
69	HA, humate cemented sands, northwest Florida, station 562-5B1.	Swanson and Palacas, 1965; Nissenbaum and Kaplan, 1972.	0.97	0.59	0.014	0.00[illegible]	-25.7	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
70	HA, humate cemented sands, northwest Florida, station 562-5B2.	Swanson and Palacas, 1965.	1.01	0.49	0.014	0.007	--	--	--
71	HA, humate cemented sands, northwest Florida, station 560-1A.	Swanson and Palacas, 1965.	1.28	0.86	0.018	0.003	--	--	--
72	HA, Terra Rosa soil, Israel.	Nissenbaum and Kaplan, 1966, 1972.	1.33	--	--	0.002	-25.6	--	--
73	HA, Rendzina soil, Israel.	Nissenbaum and Kaplan, 1966, 1972.	1.19	--	--	0.002	-26.1	--	--
74	HA, Hula Peat, Israel.	Nissenbaum and Kaplan, 1966, 1972; Nissenbaum, 1974.	1.16	0.59	0.045	--	-19.2	--	-57.5
75	HA, Beaverhills soil series, Chernozemic group, Ah horizon, Alberta, Canada.	Riffaldi and Schnitzer, 1972a, 1973.	1.16	0.45	0.062	0.007	--	--	--
76	FA as above, Alberta, Canada.	Riffaldi and Schnitzer, 1972b.	1.65	0.83	0.057	0.015	--	--	--
77	Pk as above, Alberta, Canada	Riffaldi and Schnitzer, 1972b.	1.18	0.46	0.071	0.005	--	--	--
78	HA, Armadale soil series, Podzol group, Bh horizon, Prince Edward Island, Canada.	Riffaldi and Schnitzer, 1972a.	1.05	0.44	0.040	--	--	--	--
79	FA as above, Prince Edward Island, Canada	Riffaldi and Schnitzer, 1972a; Ghosh and Schnitzer, 1980.	1.08	0.68	0.014	0.002	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios H/C	O/C	N/C	S/C	Isotope Ratios ^{13}C	^{15}N	D
80	HA, volcanic ash soil group, A_1 horizon, Tottori, Japan.	Riffaldi and Schnitzer, 1972a, 1973.	0.79	0.52	0.029	0.016	--	--	--
81	HA, diluvial soil group, A_1 horizon, Shizuoka, Japan.	Riffaldi and Schnitzer, 1972a.	0.65	0.48	0.012	--	--	--	--
82	HA, mucky peat soil series, Organic (Histosol) soil group, 0-6 in. depth in soil, Quebec, Canada.	Riffaldi and Schnitzer, 1973.	1.14	0.41	0.029	0.004	--	--	--
83	HA, Armadale soil series, Podzol group, 0 horizon, Prince Edward Is., Canada.	Riffaldi and Schnitzer, 1972b.	1.27	0.41	0.019	0.002	--	--	--
84	HA, Chesnut soil group, A_1 horizon, Bahia Blanca, Argentina.	Riffaldi and Schnitzer, 1972b.	1.08	0.47	0.071	0.005	--	--	--
85	FA as above, Bahia Blanca, Argentina.	Riffaldi and Schnitzer, 1972b.	1.49	0.77	0.071	0.008	--	--	--
86	HA, Brunizem soil group, A_1 horizon, Balcarce, Argentian.	Riffaldi and Schnitzer, 1972b.	0.95	0.50	0.051	0.006	--	--	--
87	FA as above, Balcarce, Argentina.	Riffaldi and Schnitzer, 1972b.	1.65	0.70	0.051	0.005	--	--	--
88	HA, Brunizem soil group, B2 horizon, Balcarce, Argentina.	Riffaldi and Schnitzer, 1972b.	0.91	0.48	0.051	0.004	--	--	--
89	FA as above Balcarce, Argentina.	Riffaldi and Schnitzer, 1972b.	1.41	0.75	0.053	0.004	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
90	HA, Solod soil group, A_1 horizon, Balcarce, Argentina.	Riffaldi and Schnitzer, 1972b.	1.01	0.50	0.063	0.007	--	--	--
91	HA, Solonetz soil group, A_1 horizon, Balcarce, Argentina.	Riffaldi and Schnitzer, 1972b.	1.02	0.51	0.074	0.007	--	--	--
92	HA, Dysland soil series, Solod group, Ah horizon, Alberta, Canada.	Riffaldi and Schnitzer, 1972b; Khan and Schnitzer, 1972.	1.10	0.43	0.068	0.006	--	--	--
93	FA as above, Alberta, Canada.	Riffaldi and Schnitzer, 1972b.	1.77	0.91	0.048	0.007	--	--	--
94	Pk as above, Alberta, Canada.	Riffaldi and Schnitzer, 1972b.	1.34	0.48	0.078	0.007	--	--	--
95	HA, Camrose soil series, Solonetz group, Ah horizon, Alberta, Canada.	Riffaldi and Schnitzer, 1972b; Khan and Schnitzer, 1972.	0.95	0.47	0.072	0.004	--	--	--
96	FA as above, Alberta, Canada.	Riffaldi and Schnitzer, 1972b.	1.84	0.91	0.049	0.012	--	--	--
97	Pk as above, Alberta, Canada	Riffaldi and Schnitzer, 1972b.	1.37	0.45	0.083	0.006	--	--	--
98	HA, Lake Ontario, 26 m water depth.	Kemp and Wong, 1974.	1.40	0.50	0.132	--	--	--	--
99	FA as above, Lake Ontario.	Kemp and Wong, 1974.	1.17	0.66	0.151	--	--	--	--
100	HA, Lake Ontario, 225 m water depth	Kemp and Wong, 1974.	1.46	0.47	0.108	--	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
101	FA as above, Lake Ontario.	Kemp and Wong, 1974.	1.12	0.80	0.164	--	--	--	--
102	HA, Lake Erie, 10 m water depth.	Kemp and Wong, 1974.	1.35	0.50	0.116	--	--	--	--
103	FA as above, Lake Erie.	Kemp and Wong, 1974.	1.24	0.93	0.167	--	--	--	--
104	FA, B2 horizon, Podzol soil, Conway, New Hampshire.	Weber and Wilson, 1975.	0.73	0.60	0.015	--	--	--	--
105	FA, Oyster River water, New Hamp.	Weber and Wilson, 1975.	0.84	0.65	0.019	--	--	--	--
106	HA as above, Oyster River water.	Weber and Wilson, 1975.	0.83	0.57	0.034	--	--	--	--
107	FA, Jewell Pond water, acetone treatment, New Hampshire.	Weber and Wilson, 1975.	1.11	0.80	0.030	--	--	--	--
108	FA as above, butanol treatment New Hampshire.	Weber and Wilson, 1975.	1.19	0.96	0.021	--	--	--	--
109	HA as above, New Hampshire.	Weber and Wilson, 1975.	1.02	0.42	0.028	--	--	--	--
110	HA, Gray Wooded soil, O horizon, Brenton, Alberta, Canada.	Schnitzer and Gupta, 1964.	1.29	0.51	0.052	0.003	--	--	--
111	FA as above, Breton.	Schnitzer and Gupta, 1964.	1.04	0.75	0.016	0.001	--	--	--
112	FA, Gray Wooded soil, B2 horizon, Breton, Alberta, Canada.	Schnitzer and Gupta, 1964.	1.39	0.77	0.037	0.001	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
113	HA, Podzol soil, O horizon, Breton, Alberta, Canada.	Schnitzer and Gupta, 1964.	1.11	0.50	0.034	0.002	--	--	--
114	FA, Armadale profile, Podzol soil, Bh horizon, Alberta, Canada.	Schnitzer and Gupta, 1964.	0.78	0.66	0.013	0.002	--	--	--
115	HA, Armadale profile, Podzol soil group, A_0 horizon.	Schnitzer and Desjardins, 1962.	1.09	0.47	0.035	0.003	--	--	--
116	HA, Lake Haruna, Japan.	Ishiwitari, 1969.	1.28	0.49	0.086	--	--	--	--
117	HA, sandy Podzol, Bh horizon, Jutland, Denmark.	Hansen and Schnitzer, 1966.	1.21	0.47	0.024	0.004	--	--	--
118	HA, Pont Casse' soil series, Incepticols group, tropical volcanic soil, surface, Dominica.	Griffith and Schnitzer, 1975.	1.16	0.48	0.069	0.004	--	--	--
119	FA as above, Dominica.	Griffith and Schnitzer, 1975.	1.28	0.63	0.053	0.010	--	--	--
120	HA, Pont Casse' soil series, Incepticols group, tropical volcanic soil, sample 2, surface, Dominica.	Griffith and Schnitzer, 1975.	1.22	0.48	0.065	0.004	--	--	--
121	FA as above, Dominica.	Griffith and Schnitzer, 1975.	1.16	0.62	0.054	0.012	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
122	HA, La Plaine soil series, Incepticols group, tropical volcanic soil, sample 3, surface, Dominica.	Griffith and Schnitzer, 1975.	1.05	0.48	0.069	0.004	--	--	--
123	FA as above, Dominica.	Griffith and Schnitzer, 1975.	1.10	0.59	0.056	0.013	--	--	--
124	HA, La Plaine soil series, Incepticols group, tropical volcanic soil, subsurface, Dominica.	Griffith and Schnitzer, 1975.	1.13	0.48	0.054	0.006	--	--	--
125	FA as above, Dominica.	Griffith and Schnitzer, 1975.	1.17	0.72	0.039	0.014	--	--	--
126	HA, Boetica soil series, Incepticols group, tropical volcanic soil, surface, Dominica.	Griffith and Schnitzer, 1975.	1.15	0.47	0.087	0.005	--	--	--
127	FA as above, Dominica.	Griffith and Schnitzer, 1975.	1.07	0.84	0.040	0.031	--	--	--
128	HA, Boetica soil series, Incepticols group, tropical volcanic soil, subsurface, Dominica.	Griffith and Schnitzer, 1975.	1.55	0.53	0.081	0.008	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
129	FA as above, Dominica.	Griffith and Schnitzer, 1975.	1.15	0.71	0.042	0.014	--	--	--
130	FA, Armadale soil series, Podzol group, Bh horizon, 0.5 N NaOH extraction.	Schnitzer and Skinner, 1968.	0.87	0.70	0.013	0.002	--	--	--
131	FA, soil as above, 0.1 N HCl extraction.	Schnitzer and Skinner, 1968.	1.03	0.71	0.018	0.007	--	--	--
132	HA, Bainsville clay loam, Humic Gleysol soil, surface horizon, Ottawa, Canada.	Kerndorff and Schnitzer, 1980.	1.38	0.48	0.088	0.006	--	--	--
133	HA, Organic soil, the Fenlands, Methwold Norfolk, England, surface 0.5 N NaOH extraction.	Hayes and others, 1975.	1.35	0.57	0.046	--	--	--	--
134	FA as above, England.	Hayes and others, 1975.	1.60	0.79	0.082	--	--	--	--
135	HA, Armadale soil series, Spodosols group, Bh horizon, Prince Edward Is., Canada.	Senesi and others, 1977.	1.14	0.50	0.041	0.002	--	--	--
136	FA as above, Prince Edward Is.	Senesi and others, 1977.	0.85	0.65	0.009	0.014	--	--	--
137	HA, Brown Mediterranean soil type, surface, Shomera, Israel.	Chen and others, 1978.	1.08	0.39	0.073	0.008	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
138	FA as above, Shomera, Israel.	Chen and others, 1978.	1.51	0.75	0.038	0.035	--	--	--
139	HA, Brown Reddish sand soil type, surface, Rehovot, Israel.	Chen and others, 1978.	1.50	0.41	0.066	0.011	--	--	--
140	FA as above, Rehovot, Israel.	Chen and others, 1978.	1.27	0.57	0.077	0.037	--	--	--
141	HA, Terra Rossa soil type, surface Otsuni, Italy.	Chen and others, 1978.	1.24	0.51	0.073	0.009	--	--	--
142	FA as above, Otsuni, Italy.	Chen and others, 1978.	1.96	0.92	0.072	0.015	--	--	--
143	HA, Terra Rossa soil type, surface, Conversano, Italy.	Chen and others, 1978.	1.13	0.46	0.070	0.004	--	--	--
144	FA as above, Conversano, Italy.	Chen and others, 1978.	2.14	0.78	0.073	0.017	--	--	--
145	HA, Terra Rossa soil type, surface, Monopoli, Italy.	Chen and others, 1978.	1.01	0.47	0.078	0.002	--	--	--
146	FA as above, Monopoli, Italy.	Chen and others, 1978.	1.89	0.87	0.084	0.026	--	--	--
147	HA, Brown Mediterranean soil type, Sassari, Sardinia.	Chen and others, 1978.	0.99	0.49	0.056	0.002	--	--	--
148	FA as above, Sassari, Sardinia	Chen and others, 1978.	2.06	0.95	0.062	0.009	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios H/C	O/C	N/C	S/C	Isotope Ratios ^{13}C	^{15}N	D
149	HA, black Solonetz soil, Bnt_1 horizon, Alberta, Canada.	Khan, 1971.	0.87	0.44	0.055	0.003	--	--	--
150	HA, black Solonetz soil, Bnt_2 horizon, Alberta, Canada.	Khan, 1971.	0.86	0.49	0.057	0.003	--	--	--
151	HA, black Solod soil, Ae horizon, Alberta, Canada.	Khan, 1971.	1.12	0.41	0.070	0.005	--	--	--
152	HA, black Solod soil, Bnt_1 horizon, Alberta, Canada.	Khan, 1971.	1.22	0.60	0.072	0.005	--	--	--
153	HA, black Solod soil, Bnt_2 horizon, Alberta, Canada.	Khan, 1971.	0.86	0.45	0.045	0.005	--	--	--
154	HA, black Chernozem soil, Bm horizon, Alberta, Canada.	Khan, 1971.	0.89	0.45	0.051	0.006	--	--	--
155	HA, brown alluvial soil, Kfar Hassidim Israel.	Nissenbaum and Shallinger, 1974.	1.38	0.58	0.084	--	-27.0	--	--
156	FA as above, Kfar Hassidim, Israel.	Nissenbaum and Shallinger, 1974.	2.10	1.00	0.104	--	-26.1	--	--
157	HA, Terra Rossa soil, Umm-El-Zinat, Israel.	Nissenbaum and Shallinger, 1974; Nissenbaum, 1974.	1.52	0.73	0.079	--	-29.4	--	-49.7
158	FA as above, Umm-El-Zinat, Israel.	Nissenbaum and Shallinger, 1974.	2.11	0.98	0.073	--	-28.6	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
159	HA, mountain Rendzina soil, Wadi Arra, Israel.	Nissenbaum and Shallinger, 1974.	1.59	0.85	0.094	--	-26.6	--	--
160	FA as above, Wadi Arra, Israel.	Nissenbaum and Shallinger, 1974.	1.89	1.00	0.096	--	-25.6	--	--
161	HA, valley Rendzina soil, Ashdot-Ya'akov, Israel.	Nissenbaum and Shallinger, 1974.	1.35	0.75	0.091	--	-28.9	--	--
162	FA as above, Ashdot-Ya'akov.	Nissenbaum and Shallinger, 1974.	1.88	0.92	0.099	--	-28.1	--	--
163	HA, alluvial (brown) soil, Massmia, Israel.	Nissenbaum and Shallinger, 1974; Nissenbaum 1974.	1.68	0.66	0.101	--	-28.0	--	-59.5
164	FA as above, Massmia, Israel.	Nissenbaum and Shallinger, 1974	1.96	0.99	0.070	--	-26.8	--	--
165	HA, brown basaltic soil, Moledet, Israel.	Nissenbaum and Shallinger, 1974.	1.59	0.61	0.092	--	-28.4	--	--
166	FA as above, Moledet, Israel.	Nissenbaum and Shallinger, 1974.	2.04	0.92	0.077	--	-27.8	--	--
167	HA, loessial (arid) soil, Gilat, Israel.	Nissenbaum and Shallinger, 1974.	1.76	0.46	0.081	--	-25.7	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
168	FA as above, Gilat, Israel.	Nissenbaum and Shallinger, 1974.	1.90	1.19	0.086	--	-24.8	--	--
169	HA, peat, dried Hula Swamp, Israel.	Nissenbaum and Shallinger, 1974.	1.04	0.55	0.049	--	-18.0	--	--
170	FA as above, Hula Swamp, Israel.	Nissenbaum and Shallinger, 1974.	1.79	0.85	0.065	--	-17.4	--	--
171	FA, Bank's Lake water, Georgia.	Alberts and others, 1976.	1.32	0.72	0.035	--	--	--	--
172	HA, Logo Pond sediment, Georgia.	Alberts and others, 1976.	1.44	0.37	0.093	--	--	--	--
173	HA, Brunizem (Aquic Argudoll) soil, surface A_1 horizon, Illinois.	Stevenson and Goh, 1971.	0.91	0.56	0.037	--	--	--	--
174	HA, Podzol (Alfic Haplorthod) soil, illuvial B horizon, Michigan.	Stevenson and Goh, 1971.	0.23	0.41	0.016	--	--	--	--
175	FA as above, Michigan.	Stevenson and Goh, 1971.	1.09	0.74	0.042	--	--	--	--
176	FA, Podzol (Alfic Haplorthod) soil, surface A horizon, Michigan.	Stevenson and Goh, 1971.	1.01	0.74	0.049	--	--	--	--
177	HA, weathered lignite, N. Dakota.	Stevenson and Goh, 1971.	1.32	0.45	0.066	--	--	--	--
178	HA, copropelic ooze, Mud Lake, Florida.	Stevenson and Goh, 1971.	1.91	0.55	0.076	--	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
179	FA, calcareous Humic-Gley (Calcic Argaquoll) soil, surface A_1 horizon, Illinois.	Stevenson and Goh, 1971.	1.42	0.85	0.070	--	--	--	--
180	FA, organic soil, Rifle Peat, Ohio.	Stevenson and Goh, 1971.	0.70	0.75	0.042	--	--	--	--
181	HA, mixed forest soil, surface humus layer, Bearpaw Point, Lake Ithasca State Park, Minnesota.	Steurmer and others, 1978.	1.19	0.68	0.074	0.004	-26.7	+2.52	-139.5
182	Pk, as above, Minnesota.	Steurmer and others, 1978.	1.15	0.50	0.065	0.003	-28.0	+4.96	-116
183	HA, peaky muck, Staten Isl., Calif.	Steurmer and others, 1978.	0.97	0.56	0.061	0.004	-26.8	+2.7	-100.6
184	Pk as above, Calif.	Steurmer and others, 1978.	0.94	0.32	0.026	0.001	-27.2	+2.5	-140
185	HA, "paraffin dirt" soil, surface, Siglia, Antofagasta Province, Chile.	Steurmer and others, 1978.	1.73	0.62	0.134	0.041	-24.5	+14.2	--
186	Pk as above, Chile.	Steurmer and others, 1978.	1.53	0.40	0.048	0.017	-28.1	-11.4	-124
187	HA, surface sediment, small Florida lake near Gainesville.	Steurmer and others, 1978.	1.09	0.71	0.103	0.009	-24.1	+2.32	-78.1
188	Pk as above, Florida.	Steurmer and others, 1978.	0.99	0.59	0.079	0.004	-27.7	+2.4	-95

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
189	HA, surface sediment small tidal managrove swamp, Caravan Camp, Trinity Beach, Cairns, Queensland, Australia.	Steurmer and others, 1978.	0.95	0.97	0.068	0.015	-23.4	+4.31	-79.6
190	Pk as above, Australia.	Steurmer and others, 1978.	0.88	0.83	0.037	0.018	-27.1	+5.6	-100
191	HA, Blake-Bahama Basin sediment, 1.8 m depth in sediment, DSDP core 44-391B-1-2-6-13, 4963 m water depth.	Steurmer and others, 1978.	1.00	0.74	0.089	0.013	-23.1	--	--
192	HA, Tanner Basin sediment, 140 km west-southwest of Los Angeles, Calif.	Steurmer and others, 1978.	1.57	0.95	0.184	0.018	-20.7	+9.1	-105
193	Pk as above, Tanner Basin.	Steurmer and others, 1978.	1.33	0.33	0.092	0.015	-21.4	+7.3	-139
194	HA, Walvis Bay surface sediment, off southern coast Africa adjacent Namib Desert, 43 m water.	Steurmer and others, 1978.	1.54	0.86	0.162	0.030	-18.5	+10.5	-111.6
195	Pk as above. Walvis Bay	Steurmer and others, 1978.	1.36	0.87	0.122	0.031	-20.0	+9.1	-142
196	HA, Izembek Lagoon surface sediment, Bering Sea coast, Alaska Pennisula, 1 m water.	Steurmer and others, 1978.	1.39	0.44	0.129	0.018	-18.4	+7.74	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
197	HA, algal crust, Romanes Beach, Ross Island, Antarctica.	Steurmer and others, 1978.	1.37	1.03	0.149	0.010	-15.9	+18.6	-150.7
198	HA, algal mat, Laguna Mormona, Baja California, Mexico.	Steurmer and others, 1978.	1.63	0.54	0.191	0.015	-13.8	+1.7	-93.6
199	Pk as above, Laguna Mormona.	Steurmer and others, 1978.	1.54	0.30	0.109	0.014	-14.9	+4.2	-129
200	HA, surface sediment Solar Lake, sea marginal pond, Sinai coast of Gulf of Elat, Israel.	Steurmer and others, 1978.	1.69	0.66	0.150	0.031	-5.0	+2.7	-81.5
201	Pk as above, Solar Lake.	Steurmer and others, 1978.	1.58	0.74	0.151	0.032	-5.3	+1.0	-103
202	HA, Mattole River sediment, Calif.	Malcolm, 1976.	1.00	0.38	0.059	0.005	--	--	--
203	FA as above, Mattole River.	Malcolm, 1976.	1.22	0.48	0.034	0.002	--	--	--
204	HA, Mattole soil California.	Malcolm, 1976.	0.75	0.43	0.048	0.003	--	--	--
205	FA as above, Mattole soil.	Malcolm, 1976.	1.07	0.67	0.049	0.006	--	--	--
206	HA, Lakewood soil, N. Carolina.	Malcolm, 1976.	0.73	0.46	0.031	0.004	--	--	--
207	FA as above, North Carolina.	Malcolm, 1976.	0.81	0.60	0.018	0.005	--	--	--
208	HA, Fairbanks soil, Alaska	Malcolm, 1976.	0.78	0.45	0.059	0.003	--	--	--
209	FA as above, Alaska.	Malcolm, 1976.	1.12	0.65	0.047	0.004	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
210	HA, DSDP hole 379B, Black Sea, sec. 1-4, 4.5 m depth in sediment.	Huc and others, 1975.	1.07	0.42	0.058	0.014	--	--	--
211	Pk as above, 4.5 m depth.	Huc and others, 1975.	0.93	0.22	0.034	0.029	--	--	--
212	HA, DSDP hole 379B, sec. 1-4, 4.5 m depth in sediment.	Huc and others, 1975.	1.10	0.41	0.060	0.013	--	--	--
213	Pk as above, 4.5 m depth.	Huc and others, 1975.	1.04	0.23	0.033	0.042	--	--	--
214	HA, DSDP hole 379B, sec. 5-3, 77.8 m depth in sediment.	Huc and others, 1975.	1.16	0.44	0.054	0.039	--	--	--
215	HA, DSDP hole 379B, sec. 8-4, 134.3 m depth in sediment.	Huc and others, 1975.	1.06	0.43	0.056	0.013	--	--	--
216	HA, DSDP hole 379A, Black Sea, sec. 20-2, 179.6 m depth in sediment.	Huc and others, 1975.	0.85	0.45	0.049	0.015	--	--	--
217	HA, DSDP hole 379A, sec. 28-5, 260.3 m depth in sediment.	Huc and others, 1975.	1.15	0.42	0.080	0.008	--	--	--
218	HA, DSDP hole 379A, sec. 32-2, 295.2 m depth in sediment.	Huc and others, 1975.	0.99	0.47	0.049	0.032	--	--	--
219	PK as above, 295.2 m depth.	Huc and others, 1975.	0.81	0.22	0.026	0.022	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios H/C	O/C	N/C	S/C	Isotope Ratios ^{13}C	^{15}N	D
220	HA, DSDP hole 379A, sec. 34-CC, 311.0 m depth in sediment.	Huc and others, 1975.	1.05	0.45	0.055	0.020	--	--	--
221	PK as above, 311.0 m depth.	Huc and others, 1975.	0.99	0.24	0.032	0.019	--	--	--
222	HA, DSDP hole 379A, sec. 42-4, 382.2 m depth in sediment.	Huc and others, 1975.	1.18	0.43	0.050	0.018	--	--	--
223	PK as above, 382.2 m depth.	Huc and others, 1975.	1.04	0.22	0.020	0.027	--	--	--
224	HA, DSDP hole 379A, sec. 51-0, 463.0 m depth in sediment.	Huc and others, 1975.	0.95	0.48	0.055	0.017	--	--	--
225	PK as above, 463.0 m depth.	Huc and others, 1975.	0.82	0.24	0.026	0.017	--	--	--
226	HA, DSDP hole 379A, sec. 67-1, 607.1 m depth in sediment.	Huc and others, 1975.	1.09	0.35	0.043	0.016	--	--	--
227	Pk as above, 607.1 m depth.	Huc and others, 1975.	1.07	0.26	0.026	0.019	--	--	--
228	HA, DSDP hole 380A, Black Sea, sec. 31-3, 612.7 m depth in sediment.	Huc and others, 1975.	0.91	0.42	0.048	0.015	--	--	--
229	HA, DSDP hole 380A, 41-0, 703 m depth in sediment.	Huc and others, 1975.	0.93	0.35	0.057	0.010	--	--	--
230	Pk as above. 703 m depth.	Huc and others, 1975.	1.27	0.19	0.031	0.019	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios H/C	O/C	N/C	S/C	Isotope Ratios ^{13}C	^{15}N	D
231	HA, DSDP hole 380A, sec. 41-3, 712.5 m depth in sediment.	Huc and others, 1975.	0.94	0.36	0.053	0.012	--	--	--
232	PK as above, 712.5 m depth.	Huc and others, 1975.	1.26	0.19	0.032	0.016	--	--	--
233	HA, DSDP hole 380A, sec. 46-1, 750.5 m depth in sediment.	Huc and others, 1975.	1.11	0.32	0.055	0.011	--	--	--
234	Pk as above, 750.5 m depth.	Huc and others, 1975.	1.30	0.19	0.034	0.007	--	--	--
235	HA, DSDP hole 380A, sec. 57-CC, 864.5 m depth in sediment.	Huc and others, 1975.	1.24	0.29	0.046	0.021	--	--	--
236	PK as above, 864.5 m depth.	Huc and others, 1975.	1.38	0.18	0.029	0.024	--	--	--
237	HA, DSDP hole 380A, sec. 63-1, 912 m depth in sediment.	Huc and others, 1975.	1.03	0.32	0.035	0.020	--	--	--
238	HA, DSDP hole 380A, sec. 73-4, 1013 m depth in sediment.	Huc and others, 1975.	1.03	0.36	0.045	0.022	--	--	--
239	HA, DSDP hole 380A, sec. 76-3, 1040 m depth in sediment.	Huc and others, 1975.	0.98	0.34	0.038	0.019	--	--	--
240	HA, sediment from mouth of watershed, Hillman Creek, Essex County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.32	0.38	0.095	0.012			

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
241	FA as above, Hillman Creek.	Whitby and Schnitzer, 1978.	1.92	0.91	0.091	0.010	--	--	--
242	HA, sediment from mouth of watershed, Little Ausable River, Huron County, Ontario Canada.	Whitby and Schnitzer, 1978.	1.43	0.40	0.085	0.013	--	--	--
243	FA as above, Little Ausable River.	Whitby and Schnitzer, 1978.	2.09	0.98	0.101	0.009	--	--	--
244	HA, sediment from mouth of watershed, Canagagique Creek Wellington County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.45	0.42	0.087	0.013	--	--	--
245	FA as above, Canagagique Creek.	Whitby and Schnitzer, 1978.	1.92	1.01	0.097	0.009	--	--	--
246	HA, sediment from mouth of watershed, Holiday Creek, Oxford County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.35	0.42	0.092	0.012	--	--	--
247	FA as above, Holiday Creek.	Whitby and Schnitzer, 1978.	1.43	0.95	0.094	0.011	--	--	--
248	HA, sediment from mouth of watershed, North Creek, Lincoln County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.50	0.32	0.091	0.041	--	--	--
249	FA as above, North Creek.	Whitby and Schnitzer, 1978.	1.98	0.92	0.107	0.028	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios H/C	O/C	N/C	S/C	Isotope Ratios ^{13}C	^{15}N	D
250	HA, soil in watershed, Big Creek, Essex County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.40	0.48	0.055	0.007	--	--	--
251	FA as above, Big Creek.	Whitby and Schnitzer, 1978.	1.80	0.71	0.071	0.014	--	--	--
252	HA, soil in watershed, Little Ausable River, Huron County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.62	0.62	0.090	0.005	--	--	--
253	FA as above, Little Ausable River.	Whitby and Schnitzer, 1978.	1.79	0.69	0.074	0.013	--	--	--
254	HA, soil in watershed, Canagagique Creek, Wellington County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.17	0.51	0.044	0.008	--	--	--
255	FA as above, Canagagique Creek.	Whitby and Schnitzer, 1978.	1.54	0.70	0.057	0.010	--	--	--
256	HA, soil from watershed, Holiday Creek, Oxford County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.52	0.52	0.055	0.006	--	--	--
257	FA as above, Holiday Creek.	Whitby and Schnitzer, 1978.	1.79	0.78	0.079	0.011	--	--	--
258	HA, soil from watershed, North Creek, Lincoln County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.37	0.53	0.066	0.007	--	--	--
259	FA as above, North Creek.	Whitby and Schnitzer, 1978.	1.77	0.86	0.070	0.011	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
260	HA, soil from watershed, Hillman Creek, Essex County, Ontario, Canada.	Whitby and Schnitzer, 1978.	1.30	0.45	0.048	0.007	--	--	--
261	FA as above, Hillman Creek.	Whitby and Schnitzer, 1978.	1.71	0.69	0.077	0.021	--	--	--
262	HA, earth hummock soil, Brunic Turbic Cryosol soil, Ahb horizon, MacKensie River, Northwest Territories, Canada.	Schnitzer and Vendette, 1975.	1.31	0.44	0.066	0.003	--	--	--
263	FA as above, MacKensie River.	Schnitzer and Vendette, 1975.	1.35	0.70	0.020	0.013	--	--	--
264	HA, Bering Sea sediment, sample point number 619, 125-145 cm depth in sediment.	Bordovskiy, 1965.	1.32	0.42	0.034	--	--	--	--
265	HA, Bering Sea sediment, sample point number 619, 215-230 cm depth in sediment.	Bordovskiy, 1965.	1.32	0.47	0.033	--	--	--	--
266	HA, Bering Sea sediment, sample point number 619, 280-304 cm depth in sediment.	Bordovskiy, 1965.	1.29	0.45	0.031	--	--	--	--
267	HA, Bering Sea sediment, sample point number 619, 440-460 cm depth in sediment.	Bordovskiy, 1965.	1.22	0.46	0.027	--	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
268	HA, Bering Sea sediment, sample point number 619, 670-690 cm depth in sediment.	Bordovskiy, 1965.	1.19	0.47	0.028	--	--	--	--
269	HA, Bering Sea sediment, sample point number 619, 865-885 cm depth in sediment.	Bordovskiy, 1965.	1.26	0.46	0.031	--	--	--	--
270	HA, Bering Sea sediment, sample point number 619, 1250-1260 cm depth in sediment.	Bordovskiy, 1965.	1.16	0.42	0.031	--	--	--	--
271	HA, Bering Sea sediment, sample point number 619, 1340-1350 cm depth in sediment.	Bordovskiy, 1965.	1.19	0.40	0.029	--	--	--	--
272	HA, surface sediment, Bering Sea, silt-clay mud, 3451 m water depth.	Bordovskiy, 1965.	1.37	0.49	0.047	--	--	--	--
273	HA, surface sediment, Bering Sea, fine sand, 508 m water.	Bordovskiy, 1965.	1.35	0.51	0.049	--	--	--	--
274	HA, surface sediment, Bering Sea, coarse silt, 82 m water.	Bordovskiy 1965.	1.58	0.53	0.063	--	--	--	--
275	HA, surface sediment, Bering Sea, coarse silt, 67 m water.	Bordovskiy, 1965.	1.73	0.62	0.049	--	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
276	HA, Bering Sea sediment, sample point number 1532, 5-15 cm depth in sediment.	Bordovskiy, 1965.	1.62	0.54	0.031	--	--	--	--
277	HA, Bering Sea sediment, sample point number 1532, 50-62 cm depth in sediment.	Bordovskiy, 1965.	1.49	0.54	0.031	--	--	--	--
278	HA, Bering Sea sediment, sample point number 1532, 120-130 cm depth in sediment.	Bordovskiy, 1965.	1.36	0.48	0.260	--	--	--	--
279	HA, Bering Sea sediment, sample point number 1532, 183-198 cm depth in sediment.	Bordovskiy, 1965.	1.39	0.46	0.043	--	--	--	--
280	HA, brown soil on granite (Typic Xerochrept), A_1 horizon, Huelva Province, Spain.	Saiz-Jimenez and others, 1979.	1.34	0.57	0.068	--	--	--	--
281	FA as above, Spain.	Saiz-Jimenez and others, 1979.	1.29	0.69	0.047	--	--	--	--
282	Pk as above, Spain.	Saiz-Jimenez and others, 1979.	1.43	0.46	0.065	--	--	--	--
283	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 2, 0 m depth in sediment.	Debyser and others, 1977b.	1.29	0.45	0.078	0.016	--	--	--
284	Pk as above, 0 m depth.	Debyser and others, 1977b.	1.08	0.25	0.027	0.017	--	--	--

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Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
285	HA, Sea of Norway sediments, Orgon 1 cruise, core KL 2, 0.50 m depth in sediment.	Debyser and others, 1977b.	1.36	0.47	0.074	0.021	--	--	--
286	HA, Sea of Norway sediments, Orgon 1 cruise, core KL 2, 0.75 m depth in sediment.	Debyser and others, 1977b.	1.30	0.46	0.078	0.026	--	--	--
287	HA, Sea of Norway sediments, Orgon 1 cruise, core KL 2, 1.0 m depth in sediment.	Debyser and others, 1977b.	1.32	0.47	0.081	0.024	--	--	--
288	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 2, 1.25 m depth in sediment.	Debyser and others, 1977b.	1.30	0.50	0.080	0.014	--	--	--
289	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 2, 1.50 m depth in sediment.	Debyser and others, 1977b.	1.35	0.49	0.088	--	--	--	--
290	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 2, 1.75 m depth in sediment.	Debyser and others, 1977b.	1.35	0.44	0.080	--	--	--	--
291	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 2, 2.00 m depth in sediment.	Debyser and others, 1977b.	1.32	0.48	0.075	0.017	--	--	--
292	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 2, 2.50 m depth in sediment.	Debyser and others, 1977b.	1.27	0.46	0.068	0.015	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
293	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 2, 3.00 m depth in sediment.	Debyser and others, 1977b.	1.30	0.52	0.080	0.016	--	--	--
294	Pk as above, 3.00 m depth.	Debyser and others, 1977b.	1.03	0.25	0.029	0.047	--	--	--
295	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 5, 0.0 m depth in sediment.	Debyser and others, 1977b.	1.35	0.49	0.091	--	--	--	--
296	PK as above, 0.0 m depth.	Debyser and others, 1977b.	0.94	0.22	0.029	0.015	--	--	--
297	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 5, 2.00 m depth in sediment.	Debyser and others, 1977b.	1.36	0.47	0.083	--	--	--	--
298	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 5, 4.00 m depth in sediment.	Debyser and others, 1977b.	1.26	0.44	0.074	0.034	--	--	--
299	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 8, 0.0 m depth in sediment.	Debyser and others, 1977b.	1.26	0.42	0.084	0.022	--	--	--
300	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 8, 0.25 m depth in sediment.	Debyser and others, 1977b.	1.19	0.44	0.068	0.014	--	--	--
301	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 8, 0.50 m depth in sediment.	Debyser and others, 1977b.	0.62	0.58	0.031	0.013	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
302	PK, Sea of Norway sediment, Orgon 1 cruise, core KL 8, 0.90 m depth in sediment.	Debyser and others, 1977b.	1.01	0.25	0.028	0.085	--	--	--
303	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 8, 1.00 m depth in sediment.	Debyser and others, 1977b.	0.90	0.37	0.039	--	--	--	--
304	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 8, 2.00 m depth in sediment.	Debyser and others, 1977b.	0.93	0.35	0.039	--	--	--	--
305	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 8, 3.00 m depth in sediment.	Debyser and others, 1977b.	0.89	0.43	0.042	0.011	--	--	--
306	Pk as above, 3.00 m depth.	Debyser and others, 1977b.	0.76	2.23	0.016	0.012	--	--	--
307	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 10, 0.0 m depth in sediment.	Debyser and others, 1977b.	1.39	0.50	0.098	0.027	--	--	--
308	Pk as above, 0.0 m depth.	Debyser and others, 1977b.	1.02	0.26	0.042	0.048	--	--	--
309	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 10, 1.00 m depth in sediment.	Debyser and others, 1977b.	1.23	0.42	0.084	0.014	--	--	--
310	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 10, 1.50 m depth in sediment.	Debyser and others, 1977b.	1.32	0.48	0.084	0.024	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
311	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 10, 2.50 m depth in sediment.	Debyser and others, 1977b.	1.38	0.45	0.090	0.022	--	--	--
312	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 10, 3.00 m depth in sediment.	Debyser and others, 1977b.	1.45	0.53	0.089	0.019	--	--	--
313	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 10, 3.50 m depth in sediment.	Debyser and others, 1977b.	1.23	0.43	0.089	0.014	--	--	--
314	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 10, 4.50 m depth in sediment.	Debyser and others, 1977b.	1.41	0.49	0.087	0.019	--	--	--
315	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 10, 5.00 m depth in sediment.	Debyser and others, 1977b.	1.23	0.51	0.081	0.017	--	--	--
316	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 14, 0.0 m depth in sediment.	Debyser and others, 1977b.	1.52	0.67	0.095	0.020	--	--	--
317	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 14, 1.00 m depth in sediment.	Debyser and others, 1977b.	1.11	0.48	0.074	0.014	--	--	--
318	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 14, 4.00 m depth in sediment.	Debyser and others, 1977b.	1.19	0.42	0.076	0.016	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios H/C	O/C	N/C	S/C	Isotope Ratios ^{13}C	^{15}N	D
319	HA, Sea of Norway sediment, Orgon 1 cruise, core KL 14, 8.50 m depth in sediment.	Debyser and others, 1977b.	1.01	0.43	0.059	0.013	--	--	--
320	HA, peat bog, Mirochov deposit, Bohemia.	Borovec and others, 1979.	1.20	0.56	0.024	--	--	--	--
321	FA, soil	Ishiwatari, 1975.	0.84	0.65	0.094	--	--	--	--
322	HA, peat.	Ishiwatari, 1975.	1.11	0.44	0.043	--	--	--	--
323	HA, peat.	Ishiwatari, 1975.	1.19	0.40	0.015	--	--	--	--
324	FA, sediment.	Ishiwatari, 1975.	1.63	0.61	0.122	--	--	--	--
325	HA, sediment.	Ishiwatari, 1975.	1.27	0.49	0.086	--	--	--	--
326	HA, Labrador Shelf, core VC-38, 0-15 cm depth in sediment.	Rashid and Vilks, 1977.	1.56	0.61	0.068	--	--	--	--
327	HA, Labrador Shelf, core VC-38, 50-60 cm depth in sediment.	Rashid and Vilks, 1977.	1.39	0.70	0.062	--	--	--	--
328	HA, Labrador Shelf, core VC-38, 100-110 cm depth in sediment.	Rashid and Vilks, 1977.	1.48	0.69	0.056	--	--	--	--
329	HA, Labrador Shelf, core VC-38, 552-562 cm depth in sediment.	Rashid and Vilks, 1977.	1.33	0.64	0.033	--	--	--	--
330	HA, Labrador Shelf, core VC-38, 793-803 cm depth in sediment.	Rashid and Vilks, 1977.	1.57	0.74	0.033	--	--	--	--

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Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios				Isotope Ratios		
			H/C	O/C	N/C	S/C	^{13}C	^{15}N	D
331	HA, Labrador Shelf, core VC-38, 1017-1027 cm depth in sediment.	Rashid and Vilks, 1977.	1.36	0.95	0.033	--	--	--	--
332	HA, Bourgneuf Bay, France.	Dereppe and others, 1980.	1.33	0.47	0.086	0.020	--	--	--
333	HA, Podzol soil, A_1 horizon, 'La Roche aux Fees' France.	Dereppe and others, 1980.	1.05	0.61	0.032	0.006	--	--	--
334	HA, peat moss, U.S.S.R.	Dereppe and others, 1980.	1.05	0.54	0.042	0.017	--	--	--
335	HA, Orgon II cruise, sediment Cariaco Trench, off Venezuela.	Dereppe and others, 1980.	1.24	0.45	0.088	0.021	--	--	--
336	FA, Sargasso seawater.	Stuermer and Payne, 1976.	1.61	0.55	0.110	--	--	--	--
337	FA, Bh horizon, Podzol soil, Falmouth, Mass.	Stuermer and Payne, 1976.	1.15	0.71	0.009	--	--	--	--
338	HA, Neyveli lignite, South India.	Baruah and others, 1981.	0.81	0.53	0.092	0.002	--	--	--
339	HA, tributary, Satilla River flood plain, water.	Reuter and Perdue, 1981.	0.97	0.63	0.013	--	--	--	--
340	FA, water, as above.	Reuter and Perdue, 1981.	0.82	0.63	0.013	--	--	--	--
341	FA, eluted through Sephadex G50.	Reuter and Perdue, 1981.	1.03	0.55	0.022	--	--	--	--
342	FA, eluted through Sephadex G25.	Reuter and Perdue, 1981.	0.83	0.65	0.012	--	--	--	--

Sample Number	Humic Substance[1] and Location	Reference	Atomic Ratios H/C	O/C	N/C	S/C	Isotope Ratios ^{13}C	^{15}N	D
343	FA, eluted through Sephadex G15.	Reuter and Perdue, 1981.	0.88	0.67	0.014	--	--	--	--
344	FA, eluted through Sephadex G10.	Reuter and Perdue, 1981.	0.87	0.67	0.019	--	--	--	--
345	HA, air sample, particulate, station DC 2 off northwest Africa.	Simoneit, 1979.	1.02	--	--	--	-23.4	--	--
346	Pk, as above, insoluble organic fraction.	Simoneit, 1978.	1.20	--	--	--	-24.4	--	--
347	HA, air sample, particulate, composite, off western Africa.	Simoneit, 1979.	1.40	--	--	--	-21.2	--	--
348	Pk, as above.	Simoneit, 1979.	0.82	--	--	--	-22.0	--	--
349	Pk, air sample, composite Barbados.	Simoneit, 1979.	0.91	--	--	--	-21.9	--	--

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APPENDIX REFERENCES

Alberts, J. J., Schindler, J. E., Nutter, D. E., Jr., and Davis, E., 1976, Elemental, infrared-red spectrophotometric and electron-spin resonance investigations of non-chemically isolated humic material: Geochimica et Cosmochimica Acta, v. 40, p. 369-372.

Baruah, M. K., Upreti, M. C., Baishya, N. K., and Dutta, S. N., 1981, Interaction of iron with humic acid extracted from lignite: Fuel, v. 60, p. 971-974.

Bordovskiy, O. K., 1965, Accumulation and transformation of organic substances in marine sediments: Marine Geology, v. 3, p. 3-114.

Borovec, Z., Kribek, B., and Tolar, V., 1979, Sorption of uranyl by humic acids: Chemical Geology, v. 27, p. 39-46.

Brown, F. S., Baedecker, M. J., Nissenbaum, A., and Kaplan, I. R., 1972, Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - III. Changes in organic constituents of sediment: Geochimica et Cosmochimica Acta, v. 36, p. 1185-1203.

Chen, Y., Senesi, N., and Schnitzer, M., 1978, Chemical and physical characteristics of humic and fulvic acids extracted from soils of the Mediterranean region: Geoderma, v. 20, p. 87-104.

Debyser, Y., Pelet, R., and Dastillung, M., 1977a, Geochimie organique de sediments marins recents, in Campos, R., and Goni J., eds., Advances in organic geochemistry 1975: Madrid, Spain, Empressa Nacional Adaro de Investigaciones Mineras, p. 289-320.

Debyser, Y., Gadel, F., Rebeller, R., LeBlond, C., Okhimian, D., Cambon, F., Cauwet, G., and Cambon, J. P., 1977b, Etude geochimique des composes humiques et des kerogenes, in Geochimie organique des sediments marins profonds: Paris, Editions du Centre National de la Recherche Scientique, p. 247-268

Dereppe, J. M., Moreaux, C., and Debyser, Y., 1980, Investigation of marine and terrestrial humic substances by ^1H and ^{13}C nuclear magnetic resonance and infrared spectroscopy: Organic Geochemistry, v. 2, p. 117-124.

Ghosh, K., and Schnitzer, M., 1980, Macromolecular structures of humic substances: Soil Science, v. 129, p. 266-276.

Griffith, S. M., and Schnitzer, M., 1975, Analytical characteristics of humic and fulvic acids extracted from tropical volcanic soils: Soil Science Society of America Proceedings, v. 39, p. 861-867.

Hansen, E. H., and Schnitzer, M., 1966, The alkaline permanganate oxidation of Danish illuvial organic matter: Soil Science Society of America Proceedings, v. 30, p. 745-748.

Hayes, M. H. B., Swift, R. S., Wardle, R. E., and Brown, J. K., 1975, Humic materials from an organic soil: a comparison of extractants and of properties of extracts: Geoderma, v. 13, p. 231-245.

Huc, A. Y., Durand, B., and Monin J. C., 1975, Humic compounds and kerogens in cores from Black Sea sediments, Leg 42B - Holes 379A, B, and 380A, in Usher, J. L., and Supko, P., eds., Initial reports of the deep sea drilling project, v. 42, part 2: Washington, U.S. Government Printing Office, p. 737-748.

Ishiwitari, R., 1969, An estimation of the aromaticity of a lake sediment humic acid by air oxidation and evaluation of it: Soil Science, v. 107, p. 53-57.

__________, 1973, Chemical characterization of fractionated humic acids from lake and marine sediments: Chemical Geology, v. 12, p. 113-126.

__________, 1975, Chemical nature of sedimentary humic acids, in Provoledo, D., and Golterman, H. L., eds., Humic substances - their structure and function in the biosphere, Proceedings of an international meeting held

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at Nieuwerluis, the Netherlands, May 29-31, 1972: Wageningen, Netherlands, Pudoc, p. 87-107.

Kemp, A. L. W., and Mudrochova, A., 1973, The distribution and nature of amino acids and other nitrogen-containing compounds in Lake Ontario surface sediments: Geochimica et Cosmochimica Acta, v. 37, p. 2191-2206.

Kemp, A. L. W., and Wong, H. K. T., 1974, Molecular-weight distribution of humic substances from Lakes Ontario and Erie sediments: Chemical Geology, v. 14, p. 15-22.

Kerndorff, H., and Schnitzer, M., 1980, Sorption of metals of humic acid: Geochimica et Cosmochimica Acta, v. 44, p. 1701-1708.

Khan, S. U., 1971, Distribution and characteristics of organic matter extracted from the Black Solonetzic and Black Chernozemic soils of Alberta: The humic acid fraction: Soil Science, V. 112, p. 401-409.

Khan, S. U., and Schnitzer, M., 1972, Permanganate oxidation of humic acids, fulvic acids and humins extracted from Ah horizons of a Black Chernozem, a Black Solod, and a Black Solonetz soil; Canadian Journal of Soil Science, V. 52, p. 43-51.

Malcom, R. L., 1976, Method and importance of obtaining humic and fulvic acids of high purity: U. S. Geological Survey Journal of Research, v. 4, p. 37-40.

Nissenbaum, A., 1974, The organic geochemistry of marine and terrestrial humic substances: implications of carbon and hydrogen isotope studies, in Tissot, B., and Bienner, F., eds., Advances in organic geochemistry 1973: Paris, Editions Technip., p. 39-51.

Nissenbaum, A., and Kaplan, I. R., 1966, Origin of the Beeri (Israel) sulfur deposit: Chemical Geology, v. 1, p. 295-316.

Nissenbaum, A., and Kaplan, I. R., 1972, Chemical and isotopic evidence for the in situ origin of humic substances: Limnology and Oceanography, v. 17, p. 570-582.

Nissenbaum, A., and Shallinger, K. M., 1974, The distribution of the stable carbon isotope ($^{13}C/^{12}C$) in fractions of soil organic matter: Geoderma, v. 20, p. 87-104.

Otsuki, A., and Hanya, T., 1967, Some precursors of humic acid in Recent lake sediment suggested by infra-red spectra: Geochimica et Cosmochimica Acta, v. 31, p. 1505-1515.

Palacas, J. G., Swanson, V. E., and Love, A. H., 1968, Organic geochemistry of Recent sediment in the Choctawhatchee Bay, Florida - a preliminary report: U.S. Geological Survey Professional Paper 600-C, p. C97-C106.

Rashid, M. A., and King, L. H., 1969, Molecular weight distribution measurements on humic and fulvic acid fractions from marine clays on the Scotian Shelf: Geochimica et Cosmochimica Acta, v. 33, p. 147-151.

Rashid, M. A., and King, L. H., 1970, Major oxygen-containing functional groups present in humic and fulvic fractions isolated from contrasting marine environments: Geochimica et Cosmochimica Acta, v. 34, p. 193-201.

Rashid, M. A., and King, L. H., 1971, Chemical characteristics of fractionated humic acids associated with marine sediments: Chemical Geology, v. 7, p. 37-43.

Rashid, M. A., and Vilks, G., 1977, Geochemical environment of methane-producing subarctic sedimentary basins of Eastern Canada, in Campos, R., and Goni, J., eds., Advances in organic geochemistry 1975: Madrid, Spain, Empresa Nacional Adaro de Investigaciones Mineras, p. 341-356.

Reuter, J. H., and Perdue, E. M., 1981, Calculation of molecular weights of humic substances from colligative data: Application to aquatic humus and its molecular size fractions: Geochimica et Cosmochimica Acta, v. 45, p. 2017-2022.

Riffaldi, R., and Schnitzer, M., 1972a, Effects of diverse experimental conditions on ESR spectra of humic substances: Geoderma, v. 8, p. 1-10.

Riffaldi, R., and Schnitzer, M., 1972b, Electron spin resonance spectrometry of humic substances: Soil Science Society of America Proceedings, v. 36, p. 301-305.

Riffaldi, R., and Schnitzer, M., 1973, Effects of 6 N HCl hydrolysis on the analytical characteristics and chemical structure of humic acids: Soil Science, v. 115, p. 349-356.

Saiz-Jimenez, C., Haider, K., and Meuzelaar, H. L. C., 1979, Comparisons of soil organic matter and its fractions by pyrolysis mass-spectrometry: Geoderma, v. 22, p. 25-38.

Schnitzer, M., and Desjardins, J. G., 1962, Molecular and equivalent weights of the organic matter of a Podzol: Soil Science Society of America Proceedings, v. 26, p. 362-365.

Schnitzer, M., and Gupta, U. C., 1964, Some chemical characteristics of the organic matter extracted from the O and B2 horizons of a gray wooded soil: Soil Science Society of America Proceedings, v. 28, p. 374-377.

Schnitzer, M., and Skinner, S. I. M., 1968, Alkali versus acid extraction of soil organic matter: Soil Science, v. 105, p. 392-396.

Schnitzer, M., and Vendette, E., 1975, Chemistry of humic substances extracted from an Arctic soil: Canadian Journal of Soil Science, v. 55, p. 55-103.

Senesi, N., Griffith, S. M., Schnitzer, M., and Townsend, M. G., 1977, Binding of Fe^{3+} by humic materials: Geochimica et Cosmochimica Acta, v. 41, p. 969-976.

Simoneit, B. R. T., 1979, Eolian particulates from oceanic and rural areas - their lipids, fulvic and humic acids and residual carbon, in Douglas, A. G., and Maxwell, J. R., eds., Advances in organic geochemistry, 1979, Oxford, England, Pergamon Press, p. 343-352.

Stuermer, D. H., and Payne, J. R., 1976, Investigations of seawater and terrestrial humic substances with carbon-13 and proton nuclear magnetic resonance: Geochimica et Cosmochimica Acta, v. 40, p. 1109-1114.

Stuermer, D. H., Peters, K. E., and Kaplan, I. R., 1978, Source indicators of humic substances and proto-kerogen. Stable isotope ratios, elemental compositions and electron spin resonance spectra: Geochimica et Cosmochimica Acta, v. 42, p. 989-997.

Stevenson, F. J., and Goh, K. M., 1971, Infrared spectra of humic acids and related substances: Geochimica et Cosmochimica Acta, v. 35, p. 471-483.

Swanson, V. E., and Palacas, J. G., 1965, Humate in coastal sands of northwest Florida: U.S. Geological Survey Bulletin 1214-B, p. B1-B9.

Weber, J. H., and Wilson, S. A., 1975, The isolation and characterization of fulvic and humic acid from river water: Water Research, v. 9, p. 1079-1084.

Whitby, L. M., and Schnitzer, M., 1978, Humic and fulvic acids in sediments and soils of agricultural watersheds: Canadian Journal of Soil Science, v. 58, p. 167-178.

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